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CLEANING WORKS OF ART: TUNING HYDROGELS PROPERTIES BY BLENDING PVA-BASED SYSTEMS

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Abstract

The choice of the most suitable system for the cleaning of cultural heritage artifacts is a challenging issue due to the great variety of materials and textures that can be encountered during restoration. High control and selectivity are the main features that should characterize an ideal cleaning system. At present, the use of cleaning fluids confined in gelled structures is considered one of the most performing strategies to face concerns related to an excessive penetration of the liquid phase within the porous matrix of the artwork. In the last decades several gel formulations were introduced in restoration practice, most of them pertaining to class of physical gels, while, more recently, also some chemical gel formulations were adopted. Physical gels have usually a jam-like texture and permit to attain homogenous cleaning thanks to their complete adaptability and adhesion to the surface they are put in contact with. However, they present important drawbacks related to left residues after treatment. Chemical gels are characterized by strong cohesion forces, which permit their easy and complete removal and, thus, a residue-free treatment. Their cleaning performances, in terms of homogeneity, might be compromised in case that the irregularities of the surface to be treated don't permit an appropriate adhesion of the gel. Blended PVA-based hydrogels, obtained through two different synthesis methods, are innovative systems that permit both, homogenous adhesion, thanks to their mechanical adaptability, and an easy and complete removal thanks to strong cohesion forces. Hydrogel synthesis is performed through cast-drying or repeated freezing and thawing of neat or blended PVA aqueous solutions. Gelification process involves the formation of crystalline regions that act as tie-points, contributing to formation of the three-dimensional network. A physico-chemical characterization was carried out on several formulations to investigate synthesis parameters that affect the final properties of the hydrogels. Water content and free water index (FWI) were quantified through thermal analysis (DTG, DSC). The crystallinity degree was determined by means of ATR-FTIR, DSC and XRD. Information about hydrogels porosity were obtained from SEM images, while networks structure was investigated through SAXS analysis. Finally, some preliminary application tests are presented.

Contents

General background and aims

The work presented in this dissertation is set within the framework of the most recent discussions regarding the cleaning of cultural heritage artifacts. Within the procedures carried out during restoration, cleaning is considered one of the most delicate and potentially harmful operations, mainly because of its intrinsic irreversibility. For these reason a high controlled and selective action is required. Cleaning is a necessary step: it permits to restore the original appearance of the object and to remove degraded compounds, which could interact unfavorably with the materials of the artwork that need to be preserved. Moreover, it usually represents a precondition for all other interventions that are part of the restoration process, since it allows the access to the artistic surface.

In the last decades, the traditional use of "free" organic solvents for the removal of undesired materials has been more and more called into question. The main concerns are in relation to the lack of control on solvents penetration and spreading within the treated substrate, which can lead to detrimental effects (e.g. solubilization or leaching of binding medias). Moreover, high toxicity of most organic solvents raises the issue of safety within the working environment.

The use of aqueous cleaning methods and/or solvents confined within polymeric matrices such as gels has been proposed as the more effective way to deal with the above-mentioned questions (cf. references of sections 1.3 and 1.4). Currently, restorers have adopted several gel or "gel-like" formulations mainly based on the use of cellulose ethers (e.g. Klucel®, Tylose, etc.) or polyacrilic acid (e.g. Carbopol®). These gels, characterized by a jam-like texture, give good cleaning results and permit to have homogeneous cleaning results thanks to their mechanical adaptability to the surface. However, they present important drawbacks related to

left gel residues on the treated surface. Gels from polyacrilic acid or cellulose ethers belong to class of physical gels: the impossibility to attain a complete removal from the surface after treatment is related to the characteristic scarce cohesion forces of this class of gels. More recently a new class of physical gels, based on the use of polysaccharidic materials such as agar-agar or gellan gum, was introduced in restoration practice. These gels, which restorers refer to as "rigid gels", are characterized by a fixed shape and permit, thus, a residue-free treatment. Their limitations are related to their retention features, which in some cases may be not sufficient for the treatment of highly sensitive materials, and the scarce mechanical stability, that may reflect in difficult manipulation.

In the past ten years, workers at CSGI (Center for Colloids and Surface Science) have largely contributed to the development of innovative and increasingly efficient gelled systems, able to be effective and versatile and, at the same time, to overcome some of the main drawbacks related to the use of the mentioned "traditional gels" used in restoration.

The present research starts from one the most recent developments in gel technology attained at CSGI in recent years, concerning the synthesis of high retentive semi-IPN hydrogels obtained through polymerization reaction of hydoxy-ethyl-methacrylate (HEMA) in presence of polyvinylpirrolidone (PVP) (see publication list in Annex).

The second experience that inspired this work has been the internship carried out in the framework of *Progetto Pegaso* (*Regione Toscana*) and *Nanoforart* (*Seventh Framework Programme*) at the *Instituto del Patrimonio Cultural de España* (IPCE). The work at IPCE was centered on the assessment of the use of gel materials in cleaning praxis and was carried out in collaboration with experienced restoration specialists. The assessment, carried out on both, "traditional gels" (Klucel®, Carbopol®, agar-agar) and innovative p(HEMA)/PVP semi-IPN hydrogels, permitted to get a deep insight on advantages and drawbacks of each tested gel system. Moreover, this experience enabled to achieve awareness on the general

requirements for an ideal gel system for cleaning cultural heritage artifacts, which might be summarized as follows:

(i) *High retention features* to grant low diffusivity rates of the cleaning system and, thus, permit a controlled cleaning action.

(ii) *Easy and residue-free removal*, which is strictly connected to cohesion forces and mechanical properties of the gel.

(iii) *Good adhesion properties*, necessary for a homogeneous interaction and thus a uniform cleaning action, especially in case of irregular or three-dimensional surfaces.

(iv) *Versatility*, that is, adaptability to different cleaning issues.

(v) *Chemical inertness* towards the original materials composing the artifact.

In respect to already existing gel systems, the synthesis of blended PVA-based systems is addressed principally to the improvement of point (ii) and (iii). In fact, usually, it might be improbable that a system is characterized by both, good mechanical features adhesion properties. As an example, a chemical gel, with its high cohesion forces, permits a residue-free removal but might be to rigid to grant a good adhesion to the surface and thus a homogeneous cleaning result. On the other hand, a physical gel with a jam-like texture might perform a homogenous cleaning, but the scarce cohesion forces don't permit a complete removal of the gel residues.

The presented PVA-based hydrogels are highly elastic, have a high degree of mechanical adjustability and are characterized by enhanced mechanical features. Thus, they permit to achieve both, a homogenous cleaning, even on irregular or molded surfaces, and a residue-free treatment.

In this thesis two different methods for the synthesis of blended PVA-based hydrogels are presented, both involving crystallites formation that leads to network formation. Different features, such as enhanced mechanical properties or hydrophilicity, can be obtained by addition of a second polymer (polyvinilpirrolidone or polyethylene glycol).

The first part of the thesis is an overall introduction to the use of gels in restoration practice. The advantages related to different classes of gels are highlighted and the reader is provided with the general terms for the classification of gels.

The following section is focused on the fundamentals necessary for a deep understanding of the processes leading to gel formation and the mechanisms and advantages that can be attained through the blending process of polymers. The three main processes involved in the synthesis of the presented systems (polymer blending, gel formation and polymer crystallization) are detailed and then specifically addressed to PVA-based hydrogels.

The experimental section is dedicated to the description of the synthesis methods, the instrumental techniques used for characterization and the discussion of the experimental results. Finally, some application properties and preliminary cleaning tests are presented.

Part I

Introduction

Chapter 1 – Cleaning with gels

Cleaning with gels is a subject that has been receiving increasing interest in the last decades from a wide array of conservators and restorers because it permits to deal with most of the recently debated issues regarding the cleaning procedure of cultural heritage artifacts.

The aim of this chapter is to introduce to the main concerns on the use of "free" organic solvents and to the advantages that can be achieved through the use of aqueous methods coupled or hosted within gel systems. Moreover, an overview on gels whose use in restoration procedures is already well established and on the most recent developments in gel-technology research will also be provided.

References for the different materials will be given in each section, however for a more detailed and all-embracing description of the systems resulting from developments in nanoscience for conservation, the reader is referred to two recent publications (Baglioni et al., 2015; Baglioni and Chelazzi, 2013).

1.1 Cleaning cultural heritage artifacts

Cleaning represents one of the most delicate and controversial procedures during the restoration process of a cultural heritage artifact. The term "cleaning" typically refers to the operations related to the removal of grime and soil from the surface, but also to the partial or complete removal of degraded layers such as aged and yellowed varnishes, adhesives or other potentially harmful materials. Since it is a completely irreversible process, its execution implies many risks for the artwork: usually the materials to be removed and those pertaining to the artifact consist in complex layered structures of few hundred of microns, thus, a very high control

over the action of the cleaning agent is required. However, cleaning is a necessary step since it permits, on the one hand, to restore the original esthetical features and to improve the readability of the artwork, on the other hand, as stated by Bonsanti, it represents *"…the condition for the access to the surface of the artifact…"* necessary for any further intervention*: "… if there is no access to the artifact, also the conditions for other structural and conservative interventions are generally missing…"* (Bonsanti, 2002).

Through the centuries cleaning was performed through the use of a great variety of materials, mainly soaps, alimentary products (wine, vinegar, lemon juice) or even biofluids such as saliva, urine or blood. Nowadays, "free" organic solvents are the most used materials for the cleaning of artifacts, although much attention is addressed towards more innovative systems such as gels, thickeners and aqueous cleaning systems.

1.2 Cleaning with "free" solvents

Among the "traditional" materials for the cleaning of artifacts, organic solvents are probably those considered the more comfortable by restorers and conservators. The apparent ease of handling and predictability of their action, the low cost and the fair effectiveness make organic solvents being the most common cleaning tool in restoration.

However, the use of "free" organic solvents entails some drawbacks related to risks for the treated artifact and potential hazard to the health of the operator. In fact, some undesired effects such as swelling of binding media, pigment alteration, transport and re-deposition of dissolved matter through the porous matrices, may arise. Moreover, cleaning with "free" solvents implies a general lack of control in cleaning process, caused by impossibility of monitoring penetration and spreading of the solvent within the treated matrix, that can lead to removal of original "patinas" considered as historical part of the artifact, or "invisible", but essential, components of the paint layer.

Cleaning with solvents is usually carried out according to the principle of "like dissolves like", that is, selectivity of solvents action is achieved by choosing a solvent that is considered to have adequate polarity for the solubilization of the undesired layer, without affecting the underlying paint layers. However, rarely the substrate results completely inert. The most common procedures for the selection of the appropriate solvent are based on the definition of the solubility parameters of the solvent (Hansen, 2007; Teas, 1968) and on practical tests for the determination of polarity of the layer to be removed, as for instance the Feller test (Cremonesi, 1998; Feller, 1976). To assist and facilitate conservators in their approach to solvent cleaning, also interactive digital programs were created, such as the "Triasol" (Cremonesi, 1999). Nevertheless, final evaluation of selectivity is usually entrusted to simple visual analysis of the operator, obviously unable to detect possible undesired consequences on a microscopic or molecular level. Burnstock and Learner evidenced through electron microscope analysis erosion phenomena of the treated surface after removal of aged mastic varnish by means of alkaline substances (Burnstock et al., 1992). Furthermore, the removal of oxidized varnishes usually requires the use of highly polar solvents, that are know to cause swelling and leaching of low-molecular weight components of the binding medium, causing stiffening and embrittlement of the paint layers. This effect has been reported on both, oil and *tempera* paint films (Khandekar et al., 1994; Phenix and Sutherland, 2001).

In addition to the risks related to the integrity of the artifact, also high toxicity of most organic solvents needs to be considered. The high volatility of solvents coupled with the difficulty to grant safe working conditions in restorer's workshops and studios increase the risks correlated to solvents toxicity. The increased awareness on safety of the working environment resulted in seeking alternative products able to be effective and, at the same time, less harmful for the operators. As a result, much research has been carried out in the last decades on the use of aqueous cleaning systems and gels.

1.3 Aqueous methods

Aqueous methods permit both, to reduce toxicity of the cleaning systems and the to control cleaning effectiveness and the interaction with the substrate by varying the properties of the system. In the last decades, Richard Wolbers has been one of the major promoters of the use of aqueous methods for cleaning painted surfaces (Wolbers, 2000). Wolbers' aqueous approach to cleaning is mainly based on the principle that the characteristics of water as a solvent can be varied by addition of other compounds, as for instance acids and alkalis, surfactants, chelating agents or enzymes. In this way, the aqueous system becomes able to interact also with materials originally not soluble in water. Control on the action of the cleaning systems is achieved by modulating parameters such the solutions viscosity, the pH and the ionic strength. As for the use of solvents, computer programs were created and shared with the conservators' community to provide practical guidelines for the testing of the suggested aqueous cleaning systems (Stavroudis, 2009; Stavroudis et al., 2005).

A significant contribution to aqueous cleaning methods was introduced by developments of nanostructured cleaning fluids. Since the first application, in the late 1980s, of a nanostructured fluid system for the removal of wax spots from Italian Renaissance wall paintings in Florence (Borgioli et al., 1995), several systems have been developed and successfully applied. Nowadays an extended literature reporting the use of complex fluids is available, proving them to be one of the most appealing and valid alternatives to the use of solvents for the selective removal of synthetic materials (Baglioni et al., 2012, 2014; Carretti et al., 2007, 2003a).

A typical class of nanostructured fluids that has been widely used for the cleaning of cultural heritage artifacts is represented by oil-in water microemulsions. A microemulsion is defined as a "liquid, stable and homogeneous, optically transparent, isotropic and "spontaneously" formed system, comprising two liquids mutually insoluble…stabilized by at least a monolayer of amphiphilic molecules (surfactants)" (Danielsson and Lindman, 1981). In an oil-in-water microemulsion,

water represents the continuous phase; the organic solvent (*oil*) is dispersed within the aqueous phase thanks to formation of micro- or nano-sized micells that are stabilized by the presence of a surfactant. These systems are thermodynamically stable and optically transparent; the continuous phase (i.e. water) represents the major component (75-99%), while the quantities of organic components (i.e. solvents and surfactants) are reduced (0,5-15%). These matter of facts make easy understand some of the major advantages related to the use of microemulsions with respect to conventional cleaning systems: (i) oil-in water formulations require very small amounts of solvents and, thanks to aqueous medium, permit a general reduction of the evaporation rate; thus, a consistent depression of toxicity and environmental impact is achieved; (ii) spreading of solubilized material (organic coatings, wax, etc.) into the porous matrix of the artifact may be limited since the removed hydrophobic material is surrounded by the hydrophilic aqueous phase that, acting as a barrier, may prevent re-deposition within the substrate porosity; (iii) owing to their small size, nano-droplets within a microemulsion are characterized by a huge exchange surface area; such extended interface maximizes the interaction with the detrimental layer facilitating its swelling/solubilization.

Microemulsions were initially designed for the removal of aged synthetic coatings from wall paintings. In fact, the use of aqueous solutions and water-based systems is generally discouraged on water-sensitive substrates as canvas, preparation layers, paper artworks, gypsum or wood. Swelling phenomena induced by water absorption in these hydrophilic materials can lead to mechanical stress that may cause detachment of paint layers or to solubilization of water-soluble components.

However, aqueous methods can be, and actually are, successfully used for the cleaning of water-sensitive artifacts if applied in a confined form (i.e. in a gelled or thickened form), that permits to control diffusion of the liquid within the treated matrix and to confine its action at the interface.

1.4 Gels for cleaning

Confining cleaning systems within a gel network that releases them gradually onto the treated substrate, permits to address the task of removing undesired layers without affecting the materials pertaining to the artifact either chemically or physically. Currently, conservators have adopted several gel and "gel-like" formulations (e.g. thickening agents), since they permit to minimize the drawbacks related to the use of free fluids (see sections 1.2 and 1.3). In particular, advantages entailed by the confinement of cleaning fluids within gels or highly viscous matrices can be summarized as follows: (i) the increase in viscosity drastically lowers the extent and the rate of penetration into the porous substrate, thus, the cleaning action is selectively limited at the interface between the artifacts surface and the environment; (ii) high viscosity also reduces the mobility of solutes inside the gel phase, thus, the rate of solubilization is much lower with respect to solubilization with a free fluid phase; lower solubilization kinetics allow higher control on the cleaning action; (iii) interaction of the liquid phase with gels network result in a drastic decrease of in the evaporation rate, with a strong reduction of toxicity issues; (iv) gel systems are very versatile; depending on their characteristics, they can be used as carriers for both, organic solvents and aqueous methods (i.e. enzymes, chelating agents, microemulsions, etc.); (iv) gels can be used on a great variety of supports; although the use of gels was introduced specifically for the cleaning of easel paintings, nowadays they have found application on the treatment of wide array of painted supports, such as glass (Valentin et al., 1996), metals (Tomozei and Balta, 1998) and feathers (da Silveira, 1997).

A brief but comprehensive overview of the classes of gels currently used in restoration and on the most recent developments in these intriguing systems will be provided in the following sections. However, the next section will detail some of the basic concepts and definitions, in order to focus on the main classes and general features characterizing gel systems.

1.4.1 Definition and classification of gels

According to terminology of the international Union of Pure and Applied Chemistry (IUPAC), a gel is defined as a "*non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid*", (Alemán et al., 2007). In other words, gels are soft materials made up by interconnected polymer chains or colloidal particles, entrapping a consistent quantity of fluid throughout their network. As a consequence, their physical properties are in-between those of a solid and of a liquid.

Despite the conspicuous literature available and the large amount of publications, the discussion on a universally recognized definition of the term "gel" is still open. The concept of gel has emerged in the field of colloid chemistry, but owing to the numerous fields of application and the variability of the characteristics of gel systems, the classification criteria greatly depend on the reference theoretical background (i.e. chemical, physical, biological, etc.) and on considered criteria (e.g. source of the gelator, structure, functional groups, etc.). As a consequence, during the last century several definitions and classifications were proposed by the scientific community, with the aim to allow identification of the phenomenological characteristics that are common to all gel systems, independently of their composition and molecular structure.

In the mid-20s Lloyd states that the condition of the gel is "easier to recognize than to define" (Lloyd, 1926). However, a rule seems to be applicable to all gelified systems: they are " build up of two components, one of which must be a liquid, and the other of which, the gelling substance proper, often spoken as the gelator, is a solid" (Lloyd, 1926). In addition to this latter compositional requirement, Lloyd highlights that also mechanical properties characterize the condition of gel: "the gel itself has the mechanical properties of a solid, i.e. it can maintain its form under the stress of its own weight, and under any mechanical stress it shows the phenomenon of strain". Almdal (Almdal et al., 1993) proposes a definition based on the following phenomenological characteristics: (i) (gels) consist of two or more

components one of which is a liquid, present in substantial quantity and (b) they are soft, solid, or solid-like materials. The solid-like characteristics of gels are further defined in terms of the dynamic mechanical properties (Almdal et al., 1993).

Important milestones were set by the development of statistical approaches for the prediction of the gel point and the modeling of gel formation, such as the "classical statistical theory" postulated by Flory and Stockmeyer, and the "percolation model" described by Zallen and Stauffer, that will be recalled in Chapter 3, and for which the reader is referred to literature (Flory, 1953; Stauffer et al., 1982; Zallen, 2008).

Considering the intrinsic complexity and the vast array of gel classes, we will proceed focusing on the topic of this dissertation, that is, gels made up by polymers. According to IUPAC recommendations (Alemán et al., 2007) a gel network formed by polymers is described as "*a covalent polymer network, e.g., a network formed by crosslinking polymer chains or by non-linear polymerization*" or "*a polymer network formed through the physical aggregation of polymer chains, caused by hydrogen bonds, crystallization, helix formation, complexation, etc., that results in regions of local order acting as the network junction points*". This definition introduces one of the criteria of classification used for the description of gels formed by polymers, that is the nature of the interactions responsible for the formation of the 3-D network.

Fig. 1.1 shows the two main mechanisms leading to network formation. For a gel of type A, network junction points are formed thanks to different types of non-covalent interactions that are formed between the macromolecular chains. These kinds of gels are usually referred as "physical gels", since formation of cross-links involves hydrophobic, electrostatic, van der Waals interactions or hydrogen bonds. Typically, polymers like polystirenes, polyacrylates, proteins, cellulose, etc., form physical gels (Guenet, 1992). Formation of gels of type B involves chemical reactions such as polymerization and/or cross-linking, thus the three dimensional network is build up through covalent bonds and can be considered as a single giant molecule. These kinds of gels are referred as "chemical gels".

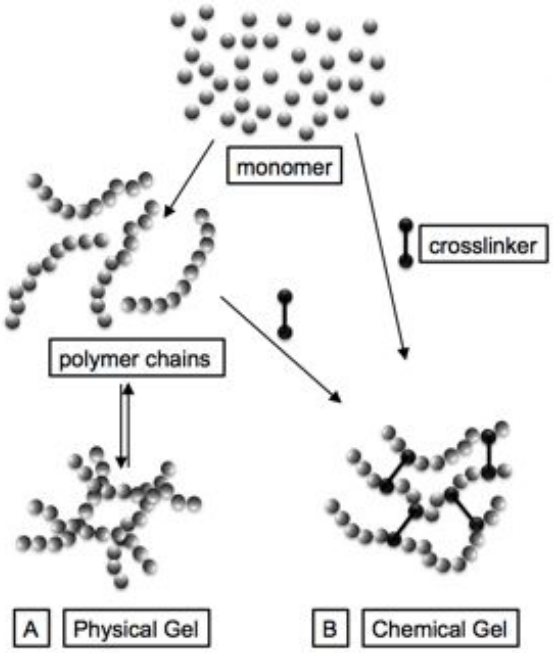

Fig. 1.1: (A) gel formation through physical association of polymer chains (physical gel); (B) gel made by polymerization and crosslinking (chemical gel). Readapted from (Baglioni and Chelazzi, 2013) .

The energies of interactions in physical gels range approximately around 1-120 kJ mol^{-1}, whereas the energies involved in covalent bonds formation are much higher, ranging from 200 to 650 kJ mol^{-1}. The characteristic energies involved in network formation are responsible for the profound difference between these two categories of gels. Owing to weak interactions existing between macromolecular chains, physical gels are thermoreversible. Increasing the temperature over a given threshold, that depends on chemical nature of both, the gellant and the liquid phase, leads to melting of the supramolecular structure: the single molecules are re-dispersed in the solvent bulk phase and a "sol" is obtained. By cooling back to original temperature a sol-gel transition occurs and the system turns back into gelled form. Differently, chemical gels are thermally irreversible systems: increasing temperature over a critical value results in the breaking of bonds and after cooling the system is not able to reproduce the original structure.

Table 1.1 summarizes the main differences between chemical and physical gels; it is important to remark that as the energy involved in physical gels increases (hydrophobic < van der Waals < hydrogen bonds < electrostatic forces) the less substantial become the differences.

	Physical gel	Chemical gel
Cross-linking	Weak interactions	Covalent bond
Thermal behavior	Reversible	Irreversible
Solvent dilution	Eventually solubilizes	Swells but not solubilizes
Shape	Mechanically adjustable	Fixed
Elastic modulus	Intermediate values	High values

Tab. 1.1: principal differences between physical and chemical gels.

Selection of the most appropriate gel system for cleaning a cultural heritage artifacts surface must keep in mind that the nature of interactions within the polymer gel network has direct consequences on application properties such as mechanical stability and gels ability to be residue-free. The strong cohesive forces in chemical gels permit to ensure that no gel residues are left on the treated surface after treatment. On the other hand, physical gels have the advantage of being mechanically adjustable, granting a perfect adhesion and, thus, a more homogeneous interaction with the treated substrate. However, physical gels often leave residues on the surface, that need to be removed with appropriate solvent systems that might cause damage to the artifacts original materials.

A second criterion used for the classification of gels is based on the fluid that can be retained by the network ("gelator") and its hydrophobic/hydrophilic features. In fact, if the gelator consists in a hydrophobic polymer, the network will equilibrate with a non-polar solvent, forming a so-called organogel. On the other hand, a hydrophilic network will swell in presence of a hydrophilic solvent. If the hydrophilic solvent is water, the system is usually referred as a hydrogel. If the fluid is not a liquid but a gas, as for instance air, the gel is called aerogel. Finally, xerogels are solid systems obtained after drying a swollen gel.

The affinity of the network for different solvents is of paramount importance for application purposes: if for instance a hydrophilic gel is immersed in a hydrophobic solvent, the network will shrink in order to minimize contact with the solvent, making the system completely unusable. As will be described in the following sections, both, organogels and hydrogels are used for the cleaning of works of art.

1.4.2 Conventional gel systems in restoration practice

The most part of gelators traditionally used for the preparation of thickened or gelled systems for the cleaning of artistic substrates belong to water-soluble polymers. Some of the systems that will be described in this section do not correspond to definition of gels in its strict sense, however, for simplicity, and since they all display the macroscopic appearance of gels, we will adopt the terminology in use among restorers.

Cellulose ethers as e.g. Klucel®, Tylose and hydroxy-propyl-cellulose represent one important and widespread class of materials for the preparation of cleaning systems in restoration procedures. These hydrophilic polymers are used to thicken water and, in some cases, polar solvents such as some alcohols. For preparation, the polymers are dispersed in the liquid phase by stirring at room temperature or under heating, and then letting rest for about one day to permit the system to reach equilibrium. The obtained jam-like system can be applied on the surface to be cleaned, exhibiting film forming and adhesive properties (see Fig. 1.2).

Cellulose ethers belong to class of physical gels; as can be seen in Fig. 1.2, their scarce cohesive forces make them prone to leaving residues on the surfaces with which they are put in contact. Due to adhesiveness of the gelling materials, left residues may be hard to remove, even after accurate rinsing, and the removal may be invasive for the original substrate (Casoli et al., 2014). The presence of cellulosic residues might increase the possibility of microbial proliferation on the surface, depending on the hydrophilicity of the substrate and on storage conditions.

Fig. 1.2: Application and removal of a Klucel® "gel" (Baglioni et al., 2015).

Another class of physicals gels commonly used as cleaning systems is based on gelation of synthetic polymers derived from polyacrilic acid (e.g. Carbopol®, Pemulens®). The use of polyacrilic acid was introduced along with the development of "solvent gels", a class of materials proposed in the late 1980s by Richard Wolbers (Wolbers et al., 1988). "Solvent gel" formulations are based on the combination of two materials, the gellant (i.e. polyacrilic acid), characterized by the presence of many carboxylic groups, and a non-ionic surfactant (Ethomeen C12 or C15) with weak basic properties. Gelation of the system occurs consequently to partial neutralization of the acidic functions of polyacrilic acid that produces negatively charged carboxylate groups that repel each other through electrostatic interactions. This effect results in a significant extension of the chains, otherwise in folded conformation, and in formation of the gelling network.

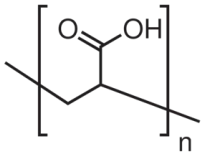

Fig. 1.3: Chemical formula of polyacrilic acid.

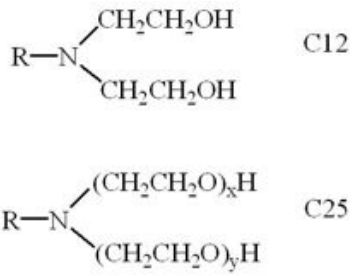

Fig. 1.4: Structure of Ethomeen C12 (top) and C25 (bottom). R is usually between 8-20 carbon atoms. For Ethomeen C25: X+Y=15 (Baglioni and Chelazzi, 2013).

The preparation of solvent gels is made through dispersion of polyacrilic acid (~1%w/w) into the solvent or solvent mixture. Then the surfactant is added (10-15% w/w) while the system is maintained under stirring. The further addition of water in small amounts (~5% w/w) produces a drastic increase in viscosity, leading to gel formation.

The two surfactants, Ethomeen C12 and C25, differ for their hydrophilic-lipophilic balance (HLB) and are thus used to induce gelation in solvents or solvent mixtures characterized by different polarities. Ethomeen C12 is used for gelation of low polarity solvents, while C25 is more suitable for highly polar solvents. In fact "solvent gels" are versatile and fair effective and, thus, among the most used gelled cleaning systems.

However, as for other mentioned physical gels for cleaning, left residues after treatment represent still the main limitation to a safe use of "solvent gels". In fact, degradation phenomena induced by the presence of residues of the non-volatile components (poymer, surfactant) are unpredictable. Risks would include a possible increase in solubility of paint layers, or in a general alteration of the paint's chemistry.

Due to these concerns, several studies have been carried out to investigate on the residue question. Stulik et al. carried out an extensive study on residue detection and degradation through accelerated aging (Stulik, 2004). Burstock and Kieslich demonstated through the use of several experimental techniques (e.g. GC-MS,

SEM) that residues of Ethomeen are left on the treated surface even after all the recommended clearance procedures were followed (Burnstock and Kieslich, 1996). Moreover, clearance recommendations for the removal of residues involve the use of free solvents or solvent mixtures, implying some of the drawbacks related to the use of "free" solvents exposed in section 1.2.

Recently, polysaccharide materials such as agar and gellan gum have been proposed for residue-free surface cleaning purposes (Campani et al., 2007; Iannuccelli and Sotgiu, 2010). Polysaccharide gellants are widely used in biomedicine, pharmacology and food industry. They are non-toxic and can be attacked by bacteria (in fact, agar is used in biology for the preparation of culture media). These materials are applied on the surfaces to be cleaned either as a highly viscous solution or as so-called "rigid gels" (see Fig. 1.5).

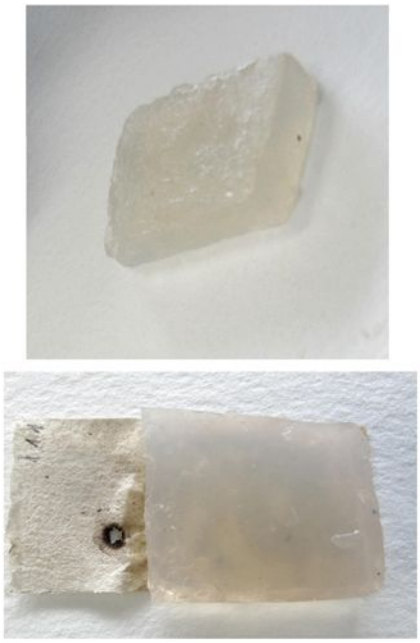

Fig. 1.5: "Rigid gels" obtained from polysaccharide materials: an agar agar gel (2%) loaded with water (Baglioni et al., 2015).

Their use as "rigid gels" permits to perform cleaning treatments leaving almost no residues, as reported in literature (Gulotta et al., 2014). The procedure for obtaining

the gels starting form polysaccharide polymers is very similar for the two considered materials: gallant is added to water (concentrations usually range from 1 to 4% w/w) and heated up to 80°C, which leads to random coil conformation of the macromolecules of the gallant. Rearrangement of the molecules upon cooling results in formation of a thermoreversible highly porous gel structure.

Agar is extracted from cell walls of red seaweed (mainly *Gelidium* and *Gracilara*) and is composed on agaropectin and agarose. Agar gels can be used with chelating agents, enzymes or surfactants at different pH values (Gulotta et al., 2014); recently they have been used also loaded with nanostructured cleaning fluids (microemulsions) for the removal of hydrophobic materials from porous surfaces (Gorel, 2010).

Gellan gum, also branded as Phytagel® and Kelcogel®, is a water-soluble polysaccharide produced by the bacterium *Pseudomonas elodea*, its repeating unit is a tetrasaccharide consisting of (1-4)-β-D-glucose, (1-4)-β-D-glucuronic acid, (1-4)-β-D-glucose and (1-4)-α-L-rhamnose. Gellan gum hydrogels used for the cleaning of artifacts are compact, visco-elastic, non-adhesive and homogeneous structures, stable at different pH values. Inannuccelli and Sotgiu studied the application of gellan gum for the cleaning of paper artifacts, observing that the gels are able to retain the dirt and that they can be removed without leaving substantial residues (Iannuccelli and Sotgiu, 2010). Moreover, the gels were loaded with enzymatic solutions or *tert*-butyl aminoborane. Gellan gels are also able to retain small amounts of polar solvents, as for instance ethanol or isopropanol.

Agar and gellan gum gels permit gentle surface cleaning or controlled humidification also on water-sensitive artifacts such as paper, however, in some cases their water retention features can be not sufficient, as for instance where leaching or loss of components (water-soluble colors or inks) might take place due to excessive wetting (Domingues et al., 2013).

1.4.3 Innovative gel systems

The aim of recent experimentation of new gel formulations, was the development of materials with enhanced properties compared to those discussed in section 1.4.2. Ongoing research has been particularly centered on development of specific key features such as the improvement of mechanical properties (to ensure ease of handling and a completely residue-free treatment) and high retentiveness (to permit a highly controlled cleaning process even on sensitive substrates).

In these frame, colloid and soft matter science has produced a significant contribution, designing a large array of advanced gels and gel-like systems of which some examples will be reported in the following paragraphs.

Strategies for the easy and complete removal of gels after cleaning treatment were draw up through the development of stimuli-responsive gels, that is, gels that can be easily and rapidly removed owing to their responsiveness to either a chemical, physical or mechanical "switch".

As an example, polyamine (i.e. polyallilamine, PAA, or polyethylenime, PEI) based rehoreversible gels, are able to be switched from a solution-type into a gel-type system through a simple chemical action (Carretti et al., 2004, 2003b). Bubbling CO_2 through a PAA solution converts it into a gallant through formation of polyallylammonium carbamate ($PAACO_2$) characterized by strong inter-chain interactions. The as formed gel is directly applicable onto a painted surface. After cleaning action rheoreversible gels are removed can be removed by simply adding in situ a small amount of a weak aqueous solution (0.05M) of acetic acid. Decarboxylation reaction promoted by the acetic acid solution reverts the gel back to a liquid, which can be soaked up with a cotton swab.

Gelled systems of PAA in 1-pentanol were used for the removal of aged varnish from a gilded 19^{th} century frame (Carretti et al., 2005), while PEI based gels proved to be effective on painted surfaces and gilded wood artifacts (Carretti et al., 2010a, 2008, 2005).

Gels responsiveness to external stimuli was further investigated by synthesis of networks able to respond to an external magnetic field. With this purpose, magnetic nanoparticles were functionalized and associated with acrylamide based gels (Bonini et al., 2008, 2007). Acrylamide hydrogels act as containers for water or aqueous solutions (e.g. microemulsions), that they are able to release in a controlled way on the surface with which they are put in contact. Thanks to magnetic properties, removal of the gel can be carried out by completely avoiding any direct handling of the gels, by means of a permanent magnet. This feature might be particularly suited in case of artistic surfaces that are extremely sensitive to mechanical stress.

Recently, chemical hydrogels with enhanced retentiveness have proved to be promising systems. They permit a safe and effective cleaning even on highly water-sensitive artifacts, providing at the same time completely residue-free results. Semi-interpenetrating networks (semi-IPN) were obtained by embedding poly(vinylpirrolidone) (PVP) within a poly(2-hydroxyethylmethacrylate) (p(HEMA)) network (Domingues et al., 2014, 2013). Blending p(HEMA) and PVP permit to take advantage of the best features of both polymers, that is good mechanical strength provided by p(HEMA) and high hydrophilicity characteristic of PVP. Moreover, hydrogels characteristics, as for instance water retention properties, can be tuned by varying compositional ratios. Hydrogels are transparent and can be prepared in the shape of elastic foils that can be easily manipulated and removed from surface after cleaning (see Fig. 1.6), without leaving residues (as assessed through FT-IR analysis (Domingues et al., 2013)). Gels can be loaded (typically by immersion for at least 12h) with water or water-based nanostructured fluids (i.e. microemulsions) for the removal of both, hydrophilic surface grime (Domingues et al., 2013) or hydrophobic materials (Domingues et al., 2014). Although gels were originally designed for water-based systems, they are also able to load some polar solvents (e.g. glycols, alcohols, ethanolamine).

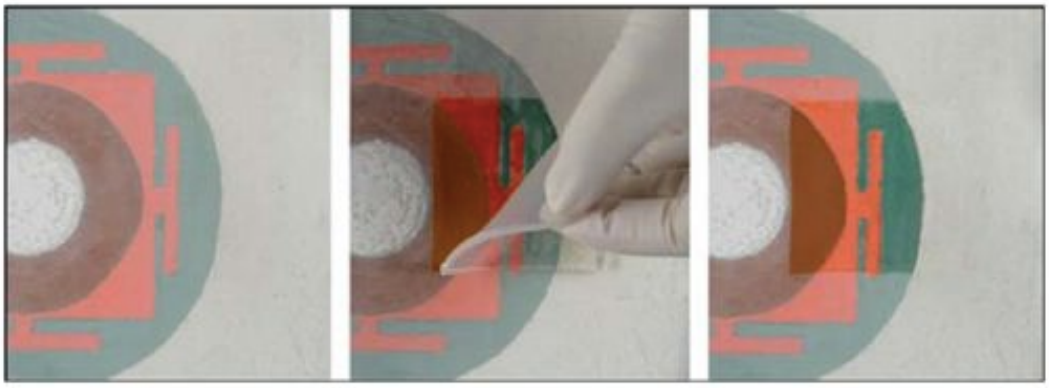

Fig 1.6: Removal of hydrophilic superficial grime using a p(HEMA)/PVP semi-IPN hydrogel loaded with water (Domingues et al., 2013).

Besides chemical gels, "gel-like" poly(vinyl alcohol) (PVA, or partially hydrolyzed poly(vinyl acetate), PVAc) based systems for the cleaning of artworks were developed (Carretti et al., 2014, 2010b, 2009). Owing to their rheological behavior they cannot be strictly defined as gels, therefore they are referred to as Highly Viscous Polymeric Dispersions (HVPD). HVPDs were obtained by adding borax to a PVA aqueous solution. The gel-like network is due to formation of cross-links between borax and PVA hydroxyl groups. The nature of cross-links depends on several factors as pH, temperature, concentration of the reagents and chemical composition of the system (Keita et al., 1995; Koike et al., 1995; Wu et al., 1990).

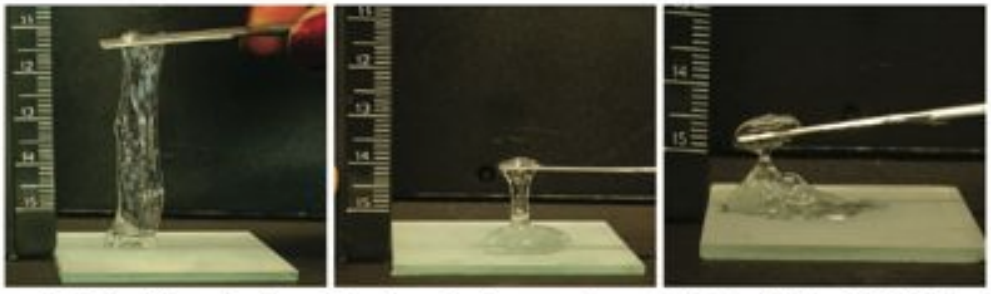

Fig. 1.7: removal of PVA-borax HVPDs with different borax content (*left, center*); comparison with properties of a traditional polyacrylic acid gel (*right*) (Carretti et al., 2009).

After use as cleaning agents, visco-elastic properties of these systems permit their removal through a simple peeling action. In fact, if compared to traditional cellose- or polyacrylic acid-based hydrogles, PVA- and PVAc-borax HVPDs respond in a

more elastic way to the mechanical action (peeling) typically involved during removal (see Fig. 1.7). This rheological feature permits a safe removal without leaving detectable residues, as assessed by FT-IR.

HVPDs are able to load different solvents including ethanol, 1-pentanol, 2-butanol, 1- and 2-propanol, acetone, cyclohexanone, *N*-methyl-pyrrolidinone and propylene carbonate. The use of partially hydrolyzed PVAc further extends the range of solvents that can be loaded, and allows the preparation of HVPDs with increased quantities of organic solvent (Angelova et al., 2011).

As an example, PVA-borax-acetone systems were used for the removal of highly degraded and darkened layers of natural resins from the "Coronation of the Virgin with Saints", an egg tempera on wood panel by Neri di Bicci (Carretti et al., 2010b).

1.5 Final remarks

It is important to recall that since cultural heritage artifacts are unique, each case study exhibits specific characteristics and a universally valid cleaning procedure does not exist. The use of gels permits to avoid some of the main drawbacks related to the use of free fluids. However some gel systems may present some disadvantages, as for example a difficult and not complete removal or insufficient retention properties to grant a controlled cleaning action. The characteristics required to an efficient gel system for the use in restoration practice may be summarized as follows:

- *High retention features* are necessary to grant low diffusivity rates of the cleaning system within the artifacts matrix and, thus, permit a controlled cleaning action. Moreover, they permit to reduce volatility of the fluid resulting in a decrease of toxicity.
- *Easy and residue-free removal*. Ease of handling and residue-free removal are usually achieved by enhancing mechanical or elastic properties. As a general rule, the stronger are interactions between the macromolecules forming the gel network, the more enhanced are gels mechanical features

owing to stronger cohesive forces. In fact, the synthesis of chemical gels represents a possible strategy to avoid residues.

- *Good adhesion properties* are necessary to grant a homogeneous interaction and thus a uniform cleaning action. Being mechanically adjustable, physical gels usually provide better adhesion; this feature is especially required on irregular or molded surfaces.
- *Versatility* in terms of adaptability to different cleaning issues, that is, the removal of the various classes of detrimental materials that might be found on artifacts surfaces. From a practical point of view, this means that an organogel must be able to load and retain an array of solvents, while a hydrogel must be able to be used in association with different aqueous cleaning methods.
- *Chemical inertness* towards the original materials composing the artifact.

It is improbable that a single gel formulation displays these features all together: the most appropriate choice for each case study will be dictated case-by-case by the specific needs and characteristics of the artifact.

In this dissertation we present the synthesis and characterization of physical PVA-based hydrogels that display at the same time good adhesion properties typical for physical gels, but enhanced mechanical features that permit a residue-less treatment of surfaces. In fact, the physical network is obtained through cross-links made up by crystallites, that is, junction points consist in ordered regions presenting a great number of hydrogen bonds. Owing to great number of interactions, strength of cross-links is comparable with those of chemical gels.

Hydrogels can be loaded with water and nanostructured fluids (microemulsions) and are, thus, suitable for the removal of different classes of materials using low-toxicity water-based cleaning systems.

Moreover the possibility of tuning hydrogels properties (e.g. hydrophilicity, porosity and cohesion) through blending with further components as poly(vinyl pyrrolidone) and poly(ethylene glycol) was also investigated.

References

Alemán, J.V., Chadwick, A.V., He, J., Hess, M., Horie, K., Jones, R.G., Kratochvíl, P., Meisel, I., Mita, I., Moad, G., Penczek, S., Stepto, R.F.T., 2007. Definitions of terms relating to the structure and processing of sols, gels, networks, and inorganic-organic hybrid materials (IUPAC Recommendations 2007). Pure Appl. Chem. 79.

Almdal, K., Dyre, J., Hvidt, S., Kramer, O., 1993. Towards a phenomenological definition of the term "gel." Polym. Gels Netw. 1, 5–17.

Angelova, L.V., Terech, P., Natali, I., Dei, L., Carretti, E., Weiss, R.G., 2011. Cosolvent gel-like materials from partially hydrolyzed poly(vinyl acetate)s and borax. Langmuir ACS J. Surf. Colloids 27, 11671–11682.

Baglioni, M., Giorgi, R., Berti, D., Baglioni, P., 2012. Smart cleaning of cultural heritage: a new challenge for soft nanoscience. Nanoscale 4, 42–53.

Baglioni, P., Berti, D., Bonini, M., Carretti, E., Dei, L., Fratini, E., Giorgi, R., 2014. Micelle, microemulsions, and gels for the conservation of cultural heritage. Adv. Colloid Interface Sci., Special Issue in honor of Bjorn Lindman 205, 361–371.

Baglioni, P., Chelazzi, D., 2013. Nanoscience for the Conservation of Works of Art: RSC. Royal Society of Chemistry, Cambridge.

Baglioni, P., Chelazzi, D., Giorgi, R., 2015. Nanotechnologies in the Conservation of Cultural Heritage - A compendium of materials and techniques. Springer, Dordrecht.

Bonini, M., Lenz, S., Falletta, E., Ridi, F., Carretti, E., Fratini, E., Wiedenmann, A., Baglioni, P., 2008. Acrylamide-Based Magnetic Nanosponges: A New Smart Nanocomposite Material. Langmuir 24, 12644–12650.

Bonini, M., Lenz, S., Giorgi, R., Baglioni, P., 2007. Nanomagnetic Sponges for the Cleaning of Works of Art. Langmuir 23, 8681–8685.

Bonsanti, G., 2002. Storia ed Etica della Pulitura, in: Colore E Conservazione: Materiali E Metodi Nel Restauro Delle Opere Policrome Mobili. Presented at the CESMAR7, Il Prato, Piazzola sul Brenta, pp. 14–15.

Borgioli, L., Caminati, G., Gabrielli, G., Ferroni, E., 1995. Removal of hydrophobic impurities from pictorial surfaces by means of heterogeneous systems. Sci. Technol. Cult. Herit. 4, 67–74.

Burnstock, A., Kieslich, T., 1996. A study of the clearance of solvent gels used for varnish removal from paintings. Presented at the Proceedings of 11th Triennial Conference, Edinburgh, Scotland, Sept 1-6, 1996, James & James, London, pp. 253–262.

Burnstock, A., Learner, T., Learner, T., Learner, T., 1992. Changes in the surface characteristics of artificially aged mastic varnishes after cleaning using alkaline reagents. Stud. Conserv. 37, 165–184.

Campani, E., Casoli, A., Cremonesi, P., Saccani, I., Signorini, E., 2007. L'uso di agarosio e agar per la preparazione di "gel rigidi" - Use of agarose and agar for preparing "rigid gels". Quaderni del Cesmar7, Il Prato. ed. Padova.

Carretti, E., Bonini, M., Dei, L., Berrie, B.H., Angelova, L.V., Baglioni, P., Weiss, R.G., 2010a. New Frontiers in Materials Science for Art Conservation: Responsive Gels and Beyond. Acc Chem Res 43, 751–760.

Carretti, E., Dei, L., Baglioni, P., 2003a. Solubilization of Acrylic and Vinyl Polymers in Nanocontainer Solutions. Application of Microemulsions and Micelles to Cultural Heritage Conservation. Langmuir 19, 7867–7872.

Carretti, E., Dei, L., Baglioni, P., Weiss, R.G., 2003b. Synthesis and Characterization of Gels from Polyallylamine and Carbon Dioxide as Gellant. J. Am. Chem. Soc. 125, 5121–5129.

Carretti, E., Dei, L., Macherelli, A., Weiss, R.G., 2004. Rheoreversible polymeric organogels: the art of science for art conservation. Langmuir ACS J. Surf. Colloids 20, 8414–8418.

Carretti, E., Dei, L., Weiss, R.G., 2005. Soft matter and art conservation. Rheoreversible gels and beyond. Soft Matter 1, 17–22.

Carretti, E., Dei, L., Weiss, R.G., Baglioni, P., 2008. A new class of gels for the conservation of painted surfaces. J. Cult. Herit. 9, 386–393.

Carretti, E., Giorgi, R., Berti, D., Baglioni, P., 2007. Oil-in-Water Nanocontainers as Low Environmental Impact Cleaning Tools for Works of Art: Two Case Studies. Langmuir 23, 6396–6403.

Carretti, E., Grassi, S., Cossalter, M., Natali, I., Caminati, G., Weiss, R.G., Baglioni, P., Dei, L., 2009. Poly(vinyl alcohol)−Borate Hydro/Cosolvent Gels: Viscoelastic Properties, Solubilizing Power, and Application to Art Conservation. Langmuir 25, 8656–8662.

Carretti, E., Matarrese, C., Fratini, E., Baglioni, P., Dei, L., 2014. Physicochemical characterization of partially hydrolyzed poly(vinyl acetate)-borate aqueous dispersions. Soft Matter 10, 4443–4450.

Carretti, E., Natali, I., Matarrese, C., Bracco, P., Weiss, R.G., Baglioni, P., Salvini, A., Dei, L., 2010b. A new family of high viscosity polymeric dispersions for cleaning easel paintings. J. Cult. Herit. 11, 373–380.

Casoli, A., Di Diego, Z., Isca, C., 2014. Cleaning painted surfaces: evaluation of leaching phenomenon induced by solvents applied for the removal of gel residues. Environ. Sci. Pollut. Res. Int.

Cremonesi, P., 1998. Un approccio più scientifico alla pulitura dei dipinti: il test di solubilità di Feller. Progetto Restauro 38–42.

Cremonesi, P., 1999. Un approccio più scientifico alla pulitura dei dipinti: Triansol, il triangolo delle solubilità, un software per il restauro. Progetto Restauro 6, 42–45.

Danielsson, I., Lindman, B., 1981. The definition of microemulsion. Colloids Surf. 3, 391–392.

Da Silveira, L., 1997. A note on the poultice cleaning of feathers using Laponite RD gel. Stud. Conserv. 42, 11–16.

Domingues, J.A.L., Bonelli, N., Giorgi, R., Fratini, E., Gorel, F., Baglioni, P., 2013. Innovative Hydrogels Based on Semi-Interpenetrating p(HEMA)/PVP Networks for the Cleaning of Water-Sensitive Cultural Heritage Artifacts. Langmuir 29, 2746–2755.

Domingues, J., Bonelli, N., Giorgi, R., Baglioni, P., 2014. Chemical semi-IPN hydrogels for the removal of adhesives from canvas paintings. Appl. Phys. A 114, 705–710.

Feller, R.L., 1976. The Relative Solvent Power Needed to Remove Various Aged Solvent Type Coatings, in: Conservation and Restoration of Pictorial Art. Bromelle and Smith, London.

Flory, P.J., 1953. Principles of Polymer Chemistry. Cornell University Press.

Gorel, F., 2010. Assessment of agar gel loaded with micro-emulsion for the cleaning of porous surfaces. CeROArt Conserv. Expo. Restaur. Obj. Art.

Guenet, J.-M., 1992. Thermoreversible gelation of polymers and biopolymers. Academic Press.

Gulotta, D., Saviello, D., Gherardi, F., Toniolo, L., Anzani, M., Rabbolini, A., Goidanich, S., 2014. Setup of a sustainable indoor cleaning methodology for the sculpted stone surfaces of the Duomo of Milan. Herit. Sci. 2, 1–13.

Hansen, C.M., 2007. Hansen Solubility Parameters: A User's Handbook, Second Edition. CRC Press.

Iannuccelli, S., Sotgiu, S., 2010. Wet treatment of works of art on paper with rigid gellan gums. Book Papaer Group Annu. 25–39.

Keita, G., Ricard, A., Audebert, R., Pezron, E., Leibler, L., 1995. The poly(vinyl alcohol)-borate system: influence of polyelectrolyte effects on phase diagrams. Polymer 36, 49–54.

Khandekar, N., Phenix, A., Sharp, J., 1994. Pilot study into the effects of solvents on artificially aged egg tempera films. The Conservator 18, 62–72.

Koike, A., Nemoto, N., Inoue, T., Osaki, K., 1995. Dynamic Light Scattering and Dynamic Viscoelasticity of Poly(vinyl alcohol) in Aqueous Borax Solutions. 1. Concentration Effect. Macromolecules 28, 2339–2344.

Lloyd, D.J., 1926. The problem of gel structure, in: Alexander, J. (Ed.), Colloid Chemistry: Theoretical and Applied. The Chemical Catalogue Company, New York, pp. 767–782.

Phenix, A., Sutherland, K., 2001. The cleaning of paintings: effects of organic solvents on oil paint films. Rev Conserv 2, 47–60.

Stauffer, D., Coniglio, A., Adam, M., 1982. Gelation and critical phenomena, in: Dušek, K. (Ed.), Polymer Networks, Advances in Polymer Science. Springer Berlin Heidelberg, pp. 103–158.

Stavroudis, C., 2009. The Modular Cleaning Program [WWW Document]. URL http://cool.conservation-us.org/byauth/stavroudis/mcp/ (accessed 12.12.14).

Stavroudis, C., Doherty, T., Wolbers, R., 2005. A New Approach to Cleaning I: Using Mixtures of Concentrated Stock Solutions and a Database to Arrive at an Optimal Acqueous Cleaning System. WAAC Newsl. 27, 17–28.

Stulik, D., 2004. Solvent Gels for the Cleaning of Works of Art: The Residue Question. Getty Publications.

Teas, J.P., 1968. Graphic analysis of resin solubilities. J. Paint Technol. 40, 19–25.

Tomozei, M., Balta, Z., 1998. La restauration d'une plaque de corselet (Iran, 17éeme siécle), in: Metal 98: Proceedings of the International Conference in Metals Conservation. Draguignan-Figanières. James & James, London, pp. 27–29.

Valentin, N., Sanchez, A., Herraez, I., 1996. Analyses of Deteriorated Spanish Glass Windows, Cleaning Methods using Gel Systems, in: Preprints of the ICOM Commitee for Conservation. Presented at the IIth triennal meeting in Edinburgh, Scotland, James & James, London, pp. 851–856.

Wolbers, R., 2000. Cleaning Painted Surfaces: Aqueous Methods. Archetype, London.

Wolbers, R., Sterman, N., Stavroudis, C., 1988. Notes for the Workshop on new Methods in the Cleaning of paintings. The Getty Conservation Institute, Marina del Rey.

Wu, W.L., Shibayama, M., Roy, S., Kurokawa, H., Coyne, L.D., Nomura, S., Stein, R.S., 1990. Physical gels of aqueous poly(vinyl alcohol) solutions: a small-angle neutron-scattering study. Macromolecules 23, 2245–2251.

Zallen, R., 2008. The Physics of Amorphous Solids. John Wiley & Sons.

Part II

Fundamentals

Chapter 2 – Polymer Blends

The present chapter has the aim to introduce to the concept of polymer blends in order to provide the reader with the basic thermodynamic concepts regarding the interaction that may occur in a blended polymer system and advantages that can be attained through blending process.

2.1 Blending Polymers

Blending polymers is a topic of great interest because it permits to produce new material systems with desirable features. Thus, much research has been done in the last decades to improve knowledge in polymer blend technology (Paul and Newman, 1978; Robeson and Robeson, 2007). In fact, polymer blends often represent a low-cost alternative to the development of new monomers and polymers, or to block and graft copolymerization, because they permit to obtain similar results with reduced research and development expense.

The possibility to match the requested properties by blending different macromolecules together is connected to *combination* of polymer properties according to concepts of *additivity* and *synergism* (Paul and Barlow, 1980).

When two polymers are mixed together, *additivity* of polymer properties means that in the resulting blend a specific property will be a weighted average in respect to that of the pure components. The averaging of properties has many potential benefits, because it permits to tune them in order to meet a specific requirement. Additivity is the most common composition correlated relationship in which polymer properties interact in a blend.

Less frequently, in a blend, a specific property of the single components may interact in a *synergic* way. That is, the maximum value of that property is larger than for the single components.

On the other hand, if the property exhibits a minimum when plotted versus blend proportions, blended polymers are called "incompatible".

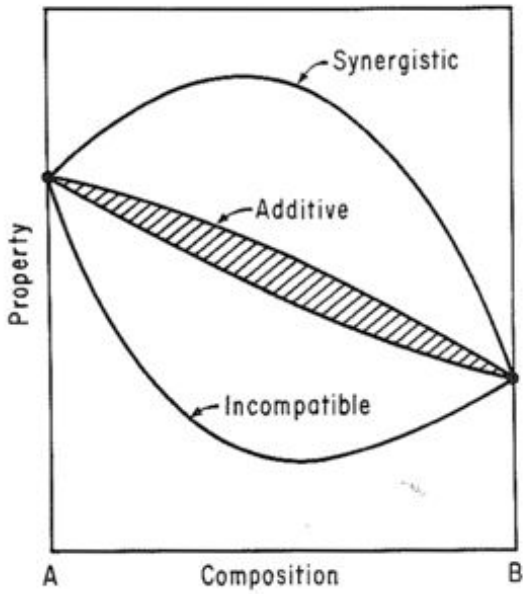

Fig 2.1: Possible effects on properties in relation to component concentration resulting from the blending of two polymers A and B (Paul and Barlow, 1980).

The situation of incompatibility, which often results in poor mechanical properties, is mainly due to scarce interfacial adhesion between the components. In fact, the most important limitation for the development of new materials through polymer blending is that most blends of high molecular weight polymers prove to be immiscible. After being mixed together, the blend components tend to separate into phases containing mainly their own kind. Low mechanical properties are often a result of this behavior combined with low physical attraction between the phase boundaries. Thus, one of the major issues in designing polymer blends is to obtain a system in which a good stress transfer within the multicomponent system is achieved. Actually, polymer incompatibility has not to be confused with immiscibility. If a blend system is able to form miscible amorphous phases, that is, a single-phase system, the components are able to mix at the molecular level.

However, strategies have been devised to address the problem of compatibility, with the result that today the vast majority of commercial polymer blends is made up by immiscible polymers. Compatibilization methods are mainly based on a proper control on phase behavior during processing, on functionalization of the polymer chains or on modification of the interface between the immiscible and incompatible components (Hobbs et al., 1988; Liu et al., 2000; Macosko, 2000; Pötschke and Paul, 2003). Compatibilized blends are often labeled as *polymer alloys*, due to some similarity to heterogeneous systems obtained in metal mixtures. *Interpenetrated polymer networks* are considered a subgroup of polymer alloys, since an excellent compatibilization is achieved.

The basic thermodynamics that concern polymer solubility and polymer-polymer miscibility will be briefly discussed, as well as the typical phase diagrams of polymer blends. Definitions for blends and interpenetrating networks will also be introduced.

2.2 Polymers in solution

2.2.1 *Thermodynamics of polymers in solution: polymer-solvent systems*

The theoretical basis to understand polymer behavior in solution was developed independently by Flory and Huggins around the mid-twentieth century (Flory, 1942; Huggins, 1942). The Flory-Huggins theory is based on a simplified model and some assumptions, but it still remains very useful for the theoretical prediction of experimental data.

The theory leads to a modification of the classical expression of the free energy of mixing ΔG_{mix}, by taking into account the different properties of a polymer solution due to the very large size of polymer solute molecules compared to solvent molecules. It also introduces the Flory-Huggins parameter χ, which permits a

quantitative description of the balance of interactions between solvent and polymer segments and to predict if a solvent is either a good or poor solvent for a given polymer.

We recall the well-known thermodynamic expression of the free energy of mixing:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{2.1}$$

Where the enthalpic and entropic variations of the solution in respect to the pure components are expressed by ΔH_{mix} and ΔS_{mix} respectively.

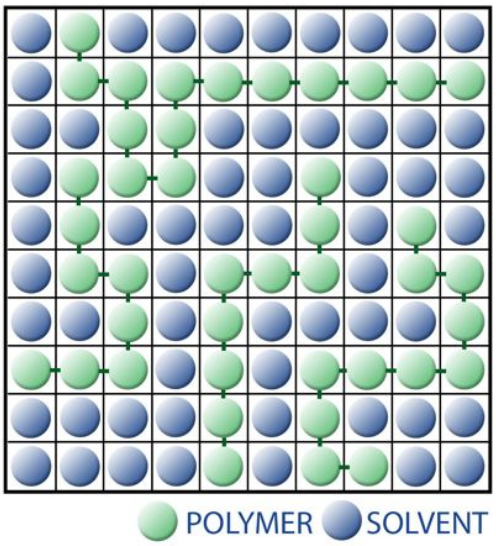

Fig 2.2: Schematic representation of the lattice model for a binary polymer-solvent system.

For what concerns the entropic term of this expression, the Flory-Huggins theory is based on a statistical approach, in which the polymer solution is described as a three-dimensional lattice (see Fig. 2.2). The entire volume is divided in N_0 cells, which can be occupied randomly by solvent molecules or by polymer segments. Each polymer segment is assumed to have the same size as a solvent molecule, thus they can be considered interchangeable within the lattice positions. Considering a monodispersed polymer, the number of segments x, contained in a polymer chain,

is given by the ratio between the molar volumes of the polymer, V_p, and the solvent, V_s:

$$x = \frac{V_p}{V_s} \tag{2.2}$$

The relation between the number of cells N_0 and the number of solvent and solute molecules, respectively N_s and N_p, is:

$$N_0 = N_s + xN_p \tag{2.3}$$

According to Boltzmann, entropy depends on the possible configurations of a system:

$$S = k\ ln\Omega \tag{2.4}$$

Where Ω is the number of possible arrangements and k the Boltzmann constant. In our special case Ω corresponds to the possible configurations that can arise by placing randomly polymer chains into the lattice and subsequently filling the voids with solvent molecules.

Statistical computations, that will not be discussed herein (for in-depth study of this subject the specific literature is recommended), permit to evaluate Ω for a polymer solution. In respect to small molecule solutions there are great limitations in the number of possible configurations due to the dimensions and the covalent bonds between polymer segments.

The expression of the entropy of mixing obtained through the Flory-Huggins theory is:

$$\Delta S_{mix} = -k\left[N_s\ lnx\frac{N_s}{N_s+xN_p} + N_p ln\frac{xN_p}{N_s+xN_p}\right] \tag{2.5}$$

Since x is related to the molar volumes (see eq. 2.2), the expression can be changed on a molar basis (*i.e.* $k = R/N_a$):

$$\Delta S_{mix} = -R\left[n_s ln\phi_s + n_p ln\phi_p\right] \quad (2.6)$$

Where n_s and n_p are the number of moles of each component and ϕ_s and ϕ_p are the volume fractions, respectively, of solvent and polymer, defined in a general form as:

$$\phi_i = \frac{n_i V_i}{\sum_i n_i V_i} \quad (2.7)$$

The expression described in (2.6) is similar to the classical expression of the entropy of mixing for small-molecule solvent-solute systems; the great innovation introduced by the Flory-Huggins theory is that volume fractions are here considered rather than molar fractions. In the case of small molecule solutes, the mole fractions and the volume fractions are essentially the same; this makes (2.6) a more general expression for the entropy of mixing.

To calculate the free energy of mixing for the solvent-polymer system, also the enthalpic term needs to be derived. The energy change related to dissolution can be associated to the fact that solvent-solvent and solute-solute interactions are replaced by solvent-solute interactions. If we name w_{ss} the energy related to solvent-solvent interactions and w_{pp} the energy related to polymer-polymer interactions, the energy associated to dissolution, *i.e.* to formation of a new interaction solvent-polymer w_{sp}, will be:

$$\Delta w = w_{sp} + \frac{1}{2}\left(w_{ss} + w_{pp}\right) \quad (2.8)$$

Obviously covalent bonds between chain segments are not included in w_{pp}; only interactions between neighboring molecules are here taken into account.

The total enthalpy of mixing will depend on the number of solvent-polymer interactions (*i.e.* sp contacts). The formation probability of a new solvent-polymer contact will depend in our lattice model on the coordination number Z (that is the

number of possible adjacent sites to a position in the lattice), and on the contact probability with sites occupied by a solvent molecule. Considering that xN_p is the total number of polymer segments, xN_pZ is the total number of sites near a polymer segment. Since the probability that any of these sites is occupied by a solvent molecule, is approximately equal to solvent volume fraction ϕ_s, the total number of contacts will be:

$$xN_pZ\phi_s = N_sZ\phi_p \tag{2.9}$$

While the enthalpy of mixing will be equal to energy change multiplied by the number of interactions:

$$\Delta H_{mix} = Z\Delta w_{sp}N_s\phi_p \tag{2.10}$$

The χ parameter is introduced to give a measure of the energetic change, in RT units, that occurs when a mole of solvent molecules is removed from pure solvent $(\phi_p = 0)$ and is immersed in a non infinite amount of polymer $\phi_p = 1$. It is defined as follows:

$$\chi = \frac{Z\Delta w}{RT} \tag{2.11}$$

This dimensionless parameter is material-specific, and it generally has positive values.

By introducing the χ parameter, the expression of the enthalpy of mixing becomes:

$$\Delta H_{mix} = RT\chi n_s\phi_p \tag{2.12}$$

According to (2.12), if χ is generally positive, the dissolution of a polymer in a solvent is generally an endothermic process.

By introducing the expressions for ΔS_{mix} and ΔH_{mix} in (2.1), the free energy of mixing for a polymer-solvent system is obtained:

$$\Delta G_{mix} = RT\left[\chi n_s \phi_p + n_s ln\phi_s + n_p ln\phi_p\right] \quad (2.13)$$

It is now clear that the dissolution of a polymer will occur depending on concentration and on sign and magnitude of χ; χ is inversely related to temperature, so increasing T will thermodynamically favor dissolution.

The value assumed by the χ parameter is a measure of the polymer-solvent interactions, as well as for the polymer-polymer interactions, thus it can predict if a solvent is good or poor for a given polymer. In general, the smaller the value of χ the greater the rates of free energy decrease during dissolution.

i) $\chi < 0$: negative values may indicate strong polar attractions between polymer and solvent;

ii) $\chi < 0.5$: selected solvent acts as a good solvent for the given polymer;

iii) $\chi = 0.5$: the so-called *theta condition*; polymer chains act as ideal chains, that is, they are not affected by wide range interactions with other polymer chains because they are compensated by the effect of the solvent; such a solvent is called *theta-solvent* and the temperature at which this condition is achieved is the *theta-temperature*;

iv) $\chi > 0.5$: selected solvent is a poor solvent and polymer will not dissolve.

2.2.2 Thermodynamics of polymers in solution: polymer-polymer systems

After the pioneering work of Flory and Huggins, thermodynamics of polymer-polymer systems have been extensively discussed by several authors (Olabisi et al., 1979; Paul and Barlow, 1980; Robeson and Robeson, 2007; Utracki et al., 1987). In this contribution we consider only some qualitative aspects, for further in-depth study we refer to specific literature.

The Flory-Huggins equation for polymer-solvent miscibility can be applied also to polymer-polymer systems, but, due to high molecular dimensions of *both* components, some additional limitation must be taken into account.

By applying the lattice model to a polymer-polymer system, it easy to compute that the number of possible arrangements within the lattice is strongly reduced if all lattice positions are occupied by long-chain molecules rather than by small molecules.

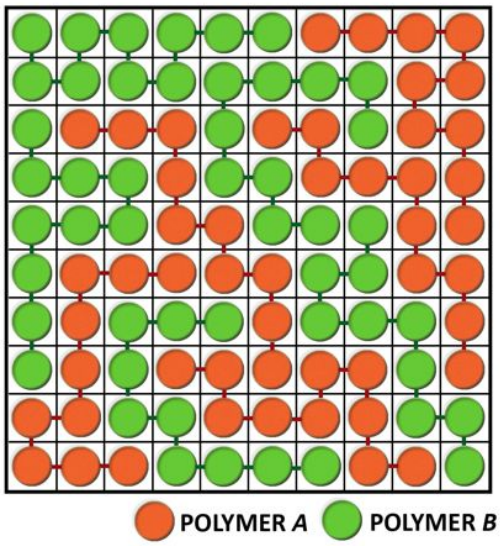

Fig 2.3: Lattice model for a binary polymer-polymer system.

The lower are the possible arrangements the lower will be the favorable contribution to free energy of mixing given by the combinatorial entropy. In the limit of very high molecular weight polymers, this contribution will be essentially zero.

For what concerns the enthalpic term, since it is related to energy changes associated to nearest neighbor contacts, it can be approximately considered independent from molecular lengths.

If a polymer-polymer system is considered, made up by non-polar components, that interact only via dispersive or van der Waals bonding between segments, the enthalpy of mixing may be estimated through the use of the Hildebrand solubility parameters (Hildebrand and Scott, 1950):

$$\Delta H_{mix} = V(\delta_1 - \delta_2)^2 \varphi_1 \varphi_2 \quad (2.14)$$

Equation (2.14) predicts always a positive value for the enthalpy of mixing, zero at the best, if δ_1 is exactly equal to δ_2. While for polymer-solvent mixtures the solubility parameter difference can be rather large, considering the insignificant contribute due to the combinatorial entropy in polymer-polymer systems, match needs to be virtually identical. That is, structural similarity between components is needed and complete miscibility is expected to be a highly unlikely event.

The solubility parameter approach gives good predictions for non-polar components, but is less suitable for highly polar or hydrogen bonding liquids or other specifically interacting molecules.

In fact, polymer types that are structurally different, but in a way that complement each other with regard to favorable energetic interactions, may mix exothermically. Thus, to achieve miscibility, a negative heat of mixing must be obtained (*i.e.* $\chi < 0$). This condition is fulfilled when strong intermolecular interactions exist between the components of the blend.

Moderate intermolecular interactions between the components results in limited miscibility, depending mainly on temperature and composition. The corresponding blend is characterized by a two-phase structure in which form and domain size depends on composition and processing conditions. Several combinations of partially miscible polymer pairs may display good mechanical, thermal, etc. properties, and can thus be useful for several applications. As already mentioned, such blends are often termed compatible or *polymer alloys*.

Partial miscibility can be explained by observing the free energy variation with the composition of the mixture (φ_i= volume fraction of component i) (Fig 2.4). Case (C) illustrates that a negative free energy of mixing does not assure complete miscibility. The maximum shown in the mid-composition range is responsible of a

splitting of a mixture of this composition into two phases, whose compositions will be given by the minima. This will result in a miscibility gap and thus, in partial miscibility.

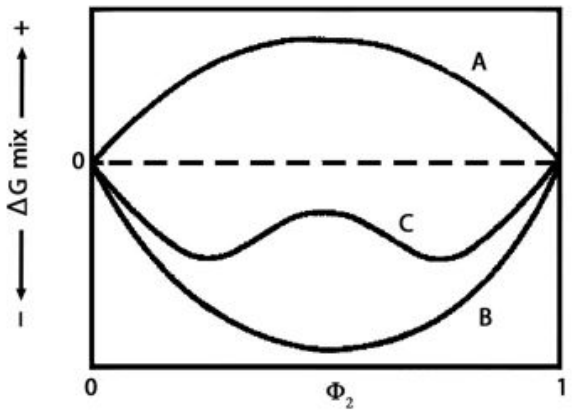

Fig 2.4: Free energy of mixing *vs.* composition of a binary mixture. Components can be (A) completely immiscible, (B) completely miscible, or (C) partially miscible (Paul and Barlow, 1980).

Thermodynamics provide the theoretical basis to predict polymer miscibility, that is, negative values for χ and ΔH_{mix} must be achieved. However, the experimental determination of the parameter χ and of ΔH_{mix} is very difficult. Values for χ may be obtained through inverse gascromatography, solvent diffusion, and composition dependence of mechanical properties or calculation from solubility parameters. For liquids ΔH_{mix} is easy determined through calorimetric methods, but its determination is more difficult in the case of viscous polymeric mixtures (Robeson, 2014).

Even though it is not a true thermodynamic property, glass transition is typically observed to investigate polymer miscibility. In amorphous polymer mixtures, variations in the glass transition temperature (T_g) after blending indicate miscibility of the components. Usually a single temperature, intermediate between the T_gs of the unmixed components, is observed. In case of partial miscibility or immiscibility, two distinct glass transitions will be observed (Fekete et al., 2005). Obviously, this

method is adequate for polymer pairs displaying well-separated glass transition temperatures.

If one of the components crystallizes, the observed T_g behavior is indicative of the state of mixing of the remaining amorphous phase (Paul and Barlow, 1980).

2.3 Phase diagrams for polymer blends

Typically, small molecule mixtures undergo phase separation primarily upon cooling, displaying an upper critical solution temperature (UCST). One of the most interesting aspects of long-chain molecules mixtures is that many miscible systems show cloud point upon heating, that is, a lower critical solution temperature (LCST) exists. Examples of phase diagrams displaying UCST and LCST are shown in Fig. 2.5.

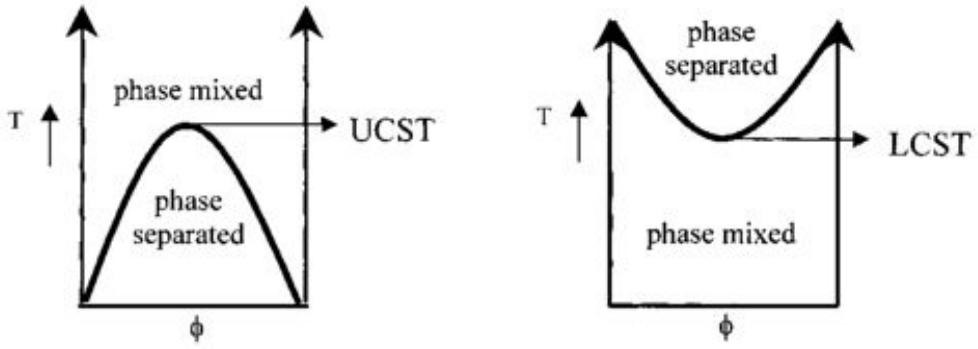

Fig 2.5: Upper critical solution temperature (UCST) and lower critical solution temperature (LCST)-type phase diagrams (Ruzette and Mayes, 2001).

The LCST behavior is not predicted by the classic Flory-Huggins theory, which is a model that does not take into account volume changes during mixing. LCST is related to finite volume variations that occur upon heating, introducing a pressure dependence of the mixing process; and to the not purely enthalpic nature of χ, that introduces additional entropic contributions that result in an increased entropy at high temperatures in the separated phases rather than in the mixed state (Sanchez

and Panayiotou, 1993). This behavior can be predicted theoretically only through modification of the original Flory-Huggins model (McMaster, 1973; Prigogine, 1957).

2.4 Phase separation in polymer solutions

Phase separation processes within miscible polymer-polymer or polymer-solvent system may occur if they are subject to temperature variation or solvent removal (evaporation or non-solvent addition). Two distinct phenomena can be observed: solid-liquid demixing and liquid-liquid demixing. Solid-liquid phase transitions occur through vitrification or crystallization of one or all the equilibrium liquid phases. Figure 2.6 illustrates a schematic equilibrium phase diagram for a solid-liquid transition in which polymer crystallization occurs.

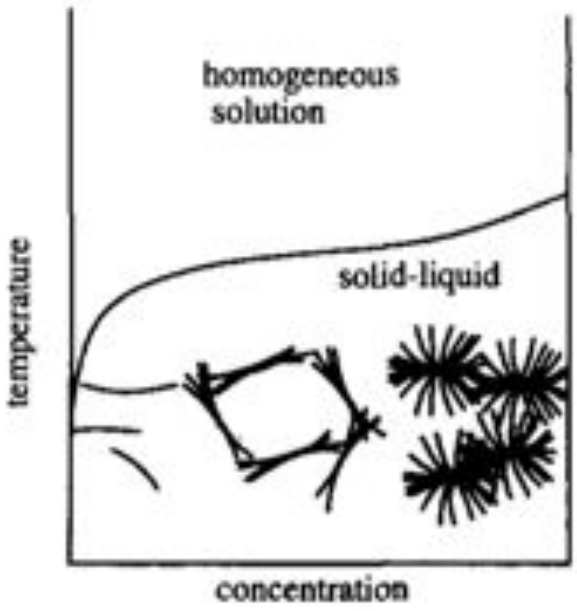

Fig 2.6: Equilibrium phase diagram for a solid-liquid transition. Different morphologies are obtained depending on polymer concentration: single crystals, lamellar stacks, spherulites (Van de Witte et al., 1996).

While solid-liquid demix generally follows the classic mechanism of nucleation and growth, the second phenomena, the liquid-liquid phase transition, is related to the thermodynamic stability of the system. Depending on where the phase boundaries are crossed, nucleation and growth or spinodal decomposition are observed. Figure 2.7 shows a typical phase diagram for a binary polymer-solvent system displaying a liquid-liquid demixing gap. It is worth to note that the phase diagram for a polymer-polymer binary system will be actually the same, except for the appearance of the demixing gap, which would be typically less asymmetric than in a polymer-solvent system.

Usually, the boundary of the liquid-liquid demixing gap is called the *binodal* or *cloud point curve*. The demixing gap is, in turn, subdivided into a region of spinodal demixing (bounded by the *spinodal*) and two regions where nucleation and growth is the predominant event. The point of coincidence of *binodal* and *spinodal* is the *critical point*.

The region located between the binodal and the spinodal is the *metastable region*, where only nucleation and growth can occur. Nucleation is an activated process forming unstable intermediate embryos. *Nuclei* are formed because of the excess of surface energy of these initial fragments of the new and more stable phase, while *nuclei* growth occurs because of the presence of concentration gradients in their immediate vicinity (Cahn, 1965).

The theory of phase separation through spinodal decomposition was described by Cahn (Cahn, 1965). This mechanism involves compositions located in the area enclosed by the spinodal curve, that is, the *unstable region*. It is best observed through undercooling of compositions that cross the phase boundary directly at the critical point. For all the remaining compositions spinodal decomposition may be observed for very high cooling rates, which prevent demixing while crossing the metastable area. If the fraction of the minor phase is sufficiently high, bicontinuous structures are formed.

At the later stages of phase separation, coarsening processes can arise to minimize interfacial energy and in time eventually two fully separated layers may be produced (see Fig 2.7).

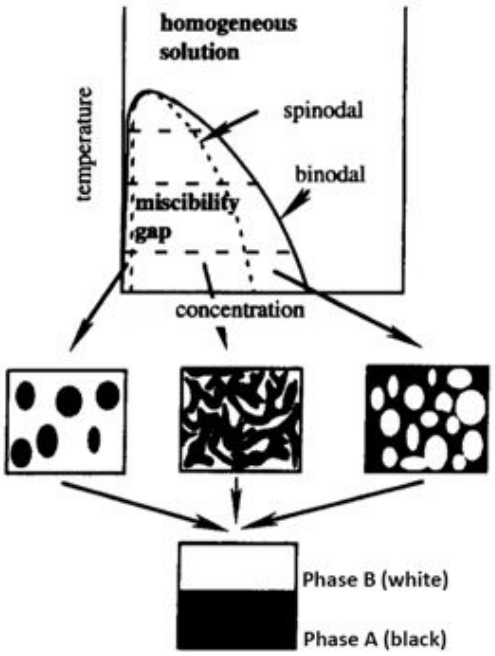

Fig 2.7: Phase diagram for a binary system showing a liquid-liquid demixing gap. Depending on temperature and concentration, different structures can be produced by the phase separation process: nucleation and growth of *phase A* (black), bicontinuous morphology due to spinodal decomposition, or nucleation and growth of *phase B* (white); coarsening may produce two fully separated layers (Van de Witte et al., 1996).

References

Cahn, J.W., 1965. Phase Separation by Spinodal Decomposition in Isotropic Systems. J. Chem. Phys. 42, 93–99.

Fekete, E., Földes, E., Pukánszky, B., 2005. Effect of molecular interactions on the miscibility and structure of polymer blends. Eur. Polym. J. 41, 727–736.

Flory, P.J., 1942. Thermodynamics of High Polymer Solutions. J. Chem. Phys. 10, 51–61.

Hildebrand, J.H., Scott, R.L., 1950. The solubility of nonelectrolytes. Reinhold Pub. Corp.

Hobbs, S.Y., Dekkers, M.E.J., Watkins, V.H., 1988. Effect of interfacial forces on polymer blend morphologies. Polymer 29, 1598–1602.

Huggins, M.L., 1942. Some Properties of Solutions of Long-chain Compounds. J. Phys. Chem. 46, 151–158. doi:10.1021/j150415a018

Liu, Q., Hedberg, E.L., Liu, Z., Bahulekar, R., Meszlenyi, R.K., Mikos, A.G., 2000. Preparation of macroporous poly (2-hydroxyethyl methacrylate) hydrogels by enhanced phase separation. Biomaterials 21, 2163–2169.

Macosko, C.W., 2000. Morphology development and control in immiscible polymer blends. Macromol. Symp. 149, 171–184. doi:10.1002/1521-3900(200001)149:1<171::AID-MASY171>3.0.CO;2-8

McMaster, L.P., 1973. Aspects of Polymer-Polymer Thermodynamics. Macromolecules 6, 760–773. doi:10.1021/ma60035a024

Olabisi, O., Robeson, L.M., Shaw, M.T., 1979. Polymer-Polymer Miscibility. Academic Press, London.

Paul, D.R., Barlow, J.W., 1980. Polymer Blends. J. Macromol. Sci. Part C Polym. Rev. 18, 109–168. doi:10.1080/00222358008080917

Paul, D.R., Newman, S., 1978. Polymer Blends. Academic Press.

Pötschke, P., Paul, D.R., 2003. Formation of Co-continuous Structures in Melt-Mixed Immiscible Polymer Blends. J. Macromol. Sci. Part C Polym. Rev. 43, 87–141. doi:10.1081/MC-120018022

Prigogine, I., 1957. The Molecular Theory of Solutions. North-Holland Publishing Company,; New York.

Robeson, L., 2014. Historical Perspective of Advances in the Science and Technology of Polymer Blends. Polymers 6, 1251–1265. doi:10.3390/polym6051251

Robeson, L., Robeson, L.M., 2007. Polymer Blends: 'A Comprehensive Review. Hanser Publications, Munich ; Cincinnati.

Ruzette, A.G., Mayes, A.M., 2001. A Simple Free Energy Model for Weakly Interacting Polymer Blends. Macromolecules 34, 1894–1907.

Sanchez, I.C., Panayiotou, C.G., 1993. Equation of State Thermodynamics of Polymer and Related Solutions, in: Sandler, S.I. (Ed.), Models for Thermodynamic and Phase Equilibria Calculations. CRC Press, New York.

Utracki, L.A., Favis, B.D., (Canada), I.M.R.I., 1987. Polymer Alloys and Blends. Industrial Materials Research Institute.

Van de Witte, P., Dijkstra, P., Van den Berg, J., Feijen, J., 1996. Phase separation processes in polymer solutions in relation to membrane formation. J. Membr. Sci. 117, 1–31.

Chapter 3 – Gelation models: phase transition and gelation in polymer solutions

In this chapter the two most common theories and models dealing with gel formation and the determination of the "gelation threshold" are discussed. First, the "classical statistical theory", proposed by Flory and Stockmeyer in the early 1950s is presented, followed by the description of the more recent "percolation model".
Moreover, some aspects that are more strictly related to physical gelation are considered, with indication of the models considering the specific interactions that are involved in this particular gelation process.

3.1 Gelation theory and models

The gelation transition has always be intriguing to many workers, however, as already mentioned in section 1.4.1, two important milestones were set by the development of statistical approaches for the prediction of the gel point. These are the "classical statistical theory" postulated by Flory and Stockmeyer (Flory, 1953), and the "percolation model" described by Zallen and Stauffer (Stauffer et al., 1982; Zallen, 2008).
In its essential features, the Flory-Sockmeyer model (F-S model) is based on multifunctional molecules between which covalent bonds are formed, to yield a network structure. In fact, the presence of multifunctional units presents nearly always the possibility of formation of infinite networks, whose presence dominates

the phenomenon of gelation (Flory, 1953). For simplicity, we consider the case of poly-functional condensation in a system made up by identical monomers with functionality $f=4$ (see Fig. 3.1(*a*), open circles represent monomers, wavy lines represent covalent bonds). In the F-S model it is assumed that the formation or not-formation of the covalent bond between monomers is a random event, which is characterized by a probability p. When the probability of formation of covalent bonds between monomers is small, the system will consist only in finite polymers (monomers, dimers, trimers, oligomers, etc.) and will exist as a *sol* phase, as depicted in Fig. 1.3 (*a*). However, if p exceeds a critical threshold value, named p_c, in addition to single molecules there exists also a single molecule, which is infinite in spatial extend ("infinite network"). This situation corresponds to *gel* phase and is described in Fig. 3.1(*b*). The weight fraction of monomers belonging to the gel molecule is zero for $p \leq p_c$ and non-zero for $p > p_c$. Using a combinatorial approach the F-S model derived an expression for the molecular weight distribution and for the critical threshold value p_c, at which the molecular weight diverges ($M_w \rightarrow \infty$, that is the *gel point*).

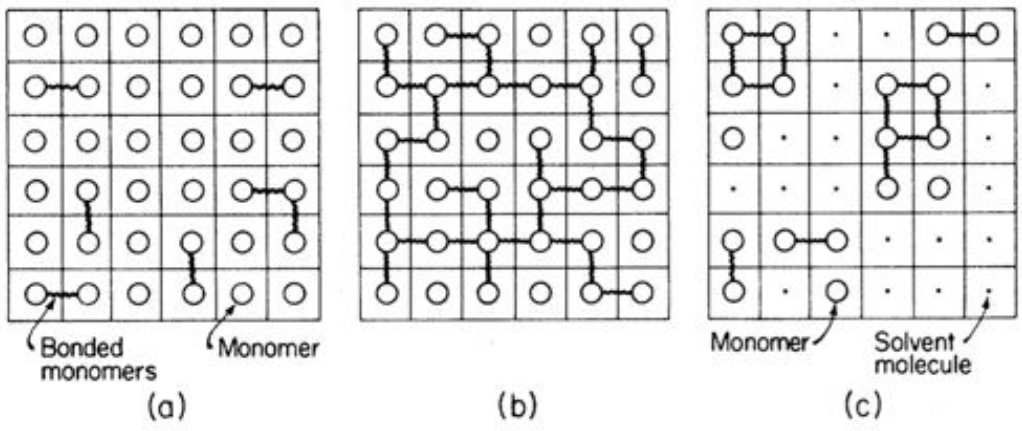

Fig. 3.1: Representation of the Flory-Stockmeyer model, where all sites are occupied by monomers, below (*a*) and over the critical threshold where $p > p_c$ and the infinite network is formed (*b*). In figure (*c*) each site can be occupied by either a monomer (circle) or solvent molecule (dot). Wavy lines correspond to chemical bonds (Coniglio et al., 1979)

The F-S model proved to be extremely versatile in providing qualitative understanding of a wide range of processes, however it is based on some simplifying assumptions:

(i) The reactivities of all functional groups of the same type are equal and independent of each other;

(ii) No intramolecular reactions between molecules (loop formation) of the same cluster are allowed;

(iii) Point-like monomers are assumed (no steric hindrance and excluded volume effects);

(iv) Solvent molecules are absent;

(v) Absence of correlation between molecules.

Especially assumptions (iv) and (v) might leave out certain features, at least in reversible gelation.

The "percolation model" takes into account both, the presence of solvent and of correlations between the molecules of the system and does not imply unlimited mobility and accessibility of all groups.

If we consider an "A site" a solvent molecule (dots in Fig. 1.3(*c*)) and a "B site" a monomer (circles in Fig. 1.3(*c*)), the particle-particle interactions can be approximated to the following four types of nearest-neighbor interactions:

$-W_{AA}$ = solvent-solvent interactions;

$-W_{AB}$= solvent-polymer interactions;

Interaction between monomers can occur in two different ways, van der Waals interactions and directional interactions leading to the formation of tie-points (e.g. covalent bonds). Thus, the monomer-monomer interactions are:

$-W_{BB}$ = monomer-monomer van der Waals interactions, with weight ρ;

-E = bonding energy between monomers, with weight $1-\rho$.

According to this description, the gel phase is defined as the phase where a non-zero finite fraction of monomers is bonded together via chemical bonds to form a macroscopic molecule (Coniglio et al., 1979).

In order to calculate the gelation threshold φ_g, the requirements for considering a pair of monomers as bonded must be defined: (i) they must be nearest neighbors and (ii) their relative interaction must be –E. The probability *p*, that a pair of neighboring monomers is bonded is given by (Coniglio et al., 1979):

$$p = \frac{(1-\rho)^{\frac{E}{kT}}}{\rho^{\frac{W_{BB}}{kT}} + (1-\rho)^{\frac{E}{kT}}} \qquad \text{(Eq. 3.1)}$$

It is worth to point out that, for simplicity, previous discussion has been restricted to systems made up by monomers and considering covalent bonds are the directional interaction established between them. Obviously, the system can be extended to systems of polymer chains of *M* monomers, as shown in the Bethe lattice in Fig. 3.2. Moreover, as stated by Kawanishi *et al.*, in thermoreversible gel systems, the directional interaction leading to network formation might be of different nature than covalent bonds (e.g. hydrogen bonds) (Kawanishi et al., 1987).

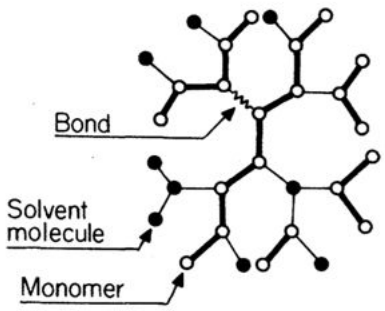

Fig. 3.2: Polymer chains in a Bethe lattice with coordination number *f*=3. Open circles represent monomers, dots are solvent molecules, wavy lines are bonds between monomers or different chains (Coniglio et al., 1979).

In the system showed in Fig. 3.2, molecules have coordination number *f*=3, that is, the number of interactions per polymer segment and per solvent molecule is equal to 3. The gelation threshold φ_g is given by:

$$\varphi_g = \frac{Rz^2\tilde{\sigma}}{[(1+R)\,\tilde{\sigma}-1]z^2+(\tilde{\sigma}-1)^2} \qquad \text{(Eq. 3.2)}$$

Where R is a parameter depending on the coordination number f and the number of monomers M; z depends on respective weight of van der Waals or directional interactions between monomers (ρ and 1-ρ); $\tilde{\sigma}$ depends on M, f and the probability of bond formation between monomers p. For the procedure to get to Eq. 3.2 the reader is referred to (Coniglio, 1976).

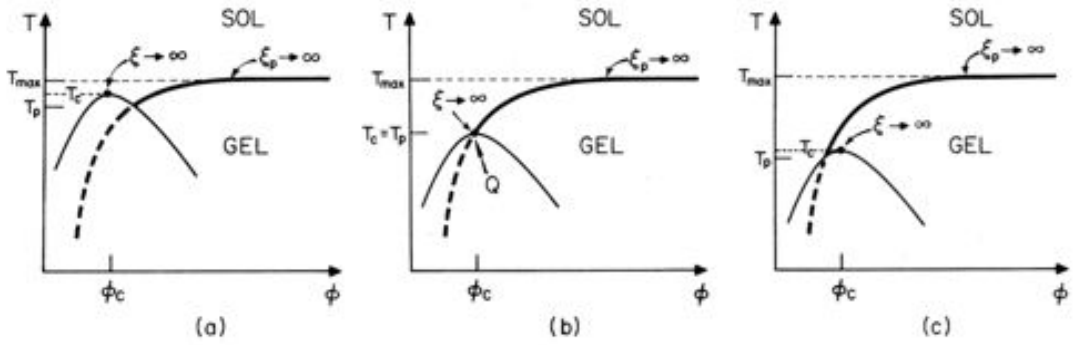

Fig. 3.3: Phase diagrams for different binary polymer-solvent systems for three different solvents. Coexistence curves and sol-gel phase boundaries are displayed. T_p is the temperature at which the sol-gel boundary crosses the coexistence curve (Coniglio, 1976).

Fig. 3.3 shows three typical schematic representations of the sol-gel phase boundary, together with the coexistence curve (binodal), for the binary monomer-solvent system, for three different solvents. The gelation curve is continued (dotted line) also within the two-phase region. Solvent parameters for the different systems have been chosen so that the consolute temperature (T_c) is in the sol region (Fig. 3.3 (*a*)), on the gelation curve (Fig. 3.3 (*b*)) or in the gel region (Fig. 3.3 (*b*)).

Some interesting features might be highlighted:

(i) There exists a limiting temperature, T_{max}, where no gelation occurs, no matter how high the monomer density is. This phenomenon is in accordance with temperature dependence of the formation probability of bonds between monomers (see Eq. 3.1), therefore $p(T_{max}) = p_c$.

(ii) For all solvents there is a temperature T_p, below the consolute temperature T_c, at which the gelation curve crosses the coexistence curve: for $T < T_p$ there is coexistence between gel and sol phase, for $T_p < T < T_c$ there are two possible gel phases.

3.2 Interactions in thermoreversible gelation

Previous section described the two main theories for the prediction of the gel point, based on statistical-mechanical considerations, which are relevant to both chemical and physical gelation processes. However, since the blended PVA-based systems presented in this dissertation pertain to thermoreversible systems, we will provide some considerations especially dedicated to physical gelation.

The large variety of systems displaying physical gelation, each with its own characteristics, has prevented unified answers to why a physical gel forms at all and to the nature of the junctions.

In thermoreversible gelation the sol-gel transition typically occurs by cooling a polymer solution, resulting in loss of its fluidity, which can be completely recovered upon heating. To do some examples with familiar polymers, this type of sol-gel transition is observed for poly(vinyl alcohol) in water, gelatin in water, poly(vinyl chloride) in dibutyl phthalate.

Basically, this behavior has been described according to three different models for the formation of tie-points within the network.

(i) The classical model by Eldridge and Ferry (Eldridge and Ferry, 1954) considers them to be a hydrogen-bond type association (HBA). In studying the melting points of gelatin solutions, Eldrige and Ferry reported the dependence of sol-gel transitions from polymer concentration and derived a relation which gives an estimate of the heat of gelation:

$$\ln c = \Delta H_m / R T_{gel-sol} \qquad \text{(Eq. 3.3)}$$

where c is the polymer concentration, ΔH_m the enthalpy of formation of one mole crosslinks and $T_{gel-sol}$ the transition temperature.

(ii) The second models considers tie-points as made up by crystallite formation (PC); this model is supported by extensive discussion on gel melting behavior in terms of thermodynamics of melting point depression (Matsuzawa et al., 1979; Ogasawara et al., 1976; Takahashi et al., 1980) and on crystallographic studies on the crystallites (Guerrero et al., 1981a, 1981b).

(iii) The third model considers liquid-liquid phase separation (LL), that is, the formation of a polymer-rich and a polymer-poor region, as the driving phenomena leading to gelation. The LL model was first proposed by Labuzinska *et al*. and Paul (Łabudzińska and Ziabicki, 1971; Paul, 1967), later Prins *et al.* (Feke and Prins, 1974; Pines and Prins, 1973) made the model clearer by applying the concept of spinodal decomposition to gelation. In this case, the network structure is interpreted in terms of connectivity of the polymer-rich phase and gelation is considered a nucleation-free process.

The phase diagram of a polymer solution will be discussed more in detail in section 5.2, where the phase transitions occurring in a poly(vinyl alcohol)/water solution will be described. It will be highlighted that, as stated by Kawanishi *et al.*, gelation is a very complex event, where the superposition of all three described processes may occur (Kawanishi et al., 1987).

References

Coniglio, A., 1976. Some cluster-size and percolation problems for interacting spins. Phys. Rev. B 13, 2194–2207.

Coniglio, A., Stanley, H., Klein, W., 1979. Site-Bond Correlated-Percolation Problem: A Statistical Mechanical Model of Polymer Gelation. Phys. Rev. Lett. 42, 518–522.

Eldridge, J.E., Ferry, J.D., 1954. Studies of the Cross-linking Process in Gelatin Gels. III. Dependence of Melting Point on Concentration and Molecular Weight. J. Phys. Chem. 58, 992–995.

Feke, G.T., Prins, W., 1974. Spinodal Phase Separation in a Macromolecular Sol → Gel Transition. Macromolecules 7, 527–530.

Flory, P.J., 1953. Principles of Polymer Chemistry. Cornell University Press.

Guerrero, S.J., Keller, A., Soni, P.L., Geil, P.H., 1981a. A study of texture in PVC gels by infrared dichroism and X-ray diffraction. J. Macromol. Sci. Part B 20, 161–166.

Guerrero, S.J., Meader, D., Keller, A., 1981b. Structure changes in PVC at high temperatures as determined from X-ray diffractometer curves. J. Macromol. Sci. Part B 20, 185–198.

Kawanishi, K., Komatsu, M., Inoue, T., 1987. Thermodynamic consideration of the sol-gel transition in polymer solutions. Polymer 28, 980–984.

Łabudzińska, A., Ziabicki, D. habil A., 1971. Effect of composition and gelation conditions on structural changes accompanying the gelation of PAN, PVA and gelatin solutions. Kolloid-Z. Z. Für Polym. 243, 21–27.

Matsuzawa, S., Yamaura, K., Maeda, R., Ogasawara, K., 1979. Melting behavior of syndiotacticity-rich poly(vinyl alcohol)-water gel. Makromol. Chem. 180, 229–239.

Ogasawara, K., Nakajima, T., Yamaura, K., Matsuzawa, S., 1976. Effect of syndiotacticity on the aqueous poly(vinyl alcohol) gel 4. X-ray diffraction analysis of gel. Colloid Polym. Sci. 254, 982–988.

Paul, D.R., 1967. Reversible gelation of acrylonitrile–vinyl acetate copolymer solutions. J. Appl. Polym. Sci. 11, 439–455.

Pines, E., Prins, W., 1973. Structure-Property Relations of Thermoreversible Macromolecular Hydrogels. Macromolecules 6, 888–895.

Stauffer, D., Coniglio, A., Adam, M., 1982. Gelation and critical phenomena, in: Dušek, K. (Ed.), Polymer Networks, Advances in Polymer Science. Springer Berlin Heidelberg, pp. 103–158.

Takahashi, A., Sakai, M., Kato, T., 1980. Melting Temperature of Thermally Reversible Gel. VI. Effect of Branching on the Sol–Gel Transition of Polyethylene Gels. Polym. J. 12, 335–341.

Zallen, R., 2008. The Physics of Amorphous Solids. John Wiley & Sons.

Chapter 4 - Polymer crystallization

Polymers physical properties are not only affected by their composition, but also by the size of their molecules and by the nature of the primary and secondary bond forces existing between them. Arrangements of the macromolecules into amorphous or crystalline domains have a great influence on physical properties like melting or softening behavior, solubility and viscosity.

This chapter addresses the topic of polymer crystallization by introducing the structure and morphology of semi-crystalline polymers. A brief overview of the different crystallization models developed during the last century and the structural characteristics that rule the crystallization process will be exposed. The thermodynamics and kinetics governing the crystallization process will not be elucidated, for which the reader is reminded to specific literature (Flory, 1949; Mandelkern, 2004).

4.1 Amorphous and crystalline regions in polymers

When considering long-chain molecules, the traditional classification into three physical states (gas, liquid, solid) does not match sufficiently the arrangements that may occur within a polymer by varying the thermodynamic variables. While phase transitions in small molecule compounds are sharp and associated with a thermodynamic equilibrium, the polymers typical states are the *glassy*, the *rubbery* and the *semi-crystalline* state, all of them being thermodynamically metastable (Krevelen and Nijenhuis, 2009; Mark, 2004).

In the crystallization process of small molecule compounds, nucleation and growth arises at temperatures in the metastable region, when stable nuclei are formed providing growth surface for crystallization. For the considered small molecule systems, each molecule participates only in one nucleus at a time, since its characteristic size is much smaller than that of a crystal nucleus. In the case of long-chain molecules, one single molecule may be able to participate in more than one of the initial nuclei, preventing the formation of a perfectly ordered structure (see Fig. 4.1).

For this reason, in the solid state most polymers consist in a combination of unordered (amorphous) and ordered regions (crystalline), which is the reason they are often termed as semi-crystalline materials.

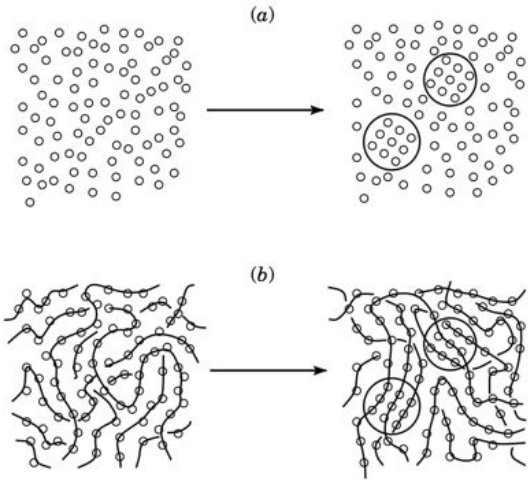

Fig. 4.1 Influence of chain connectivity on nucleation for small-molecule (a) and a long-chain molecule (b) compounds (Rice, 2004).

As reported by Carraher (Carraher, 2003), first evidence of the crystalline nature of polymers emerged in the early 1920s when Haworth and Katz observed X-ray diffraction patterns similar to those of crystalline substances respectively on elongated cellulose and stretched natural rubber.

The crystallization mechanisms, the exact nature and the resulting morphologies of the crystalline regions have been since then extensively debated and, thus, different models have been proposed during the last decades.

The presence of regions of crystallinity was first explained by the *fringed micelle model* introduced by Herman et al. in 1930 to explain the structure of gelatin (Herman et al., 1930). In the fringed micelle model, crystalline regions are formed thanks to the alignment of the macromolecular chains (either in solution or in the melt) to form small ordered regions (crystallites). The crystallites growth may occur or in the direction of the chain axis, by adjoining chain segments of molecules already part of the crystallite, or through lateral growth, by addition of further molecules. Only portions of each molecule participate in a crystallite: the same polymer chain participates to neighboring amorphous regions or to other crystallites. The respective arrangement of the crystallites is random-like, while the "fringes", connecting them through the disordered region, make them act as physical cross-links (see Fig. 4.2).

The fringed micelle model has been historically very important since it permitted to explain a great number of experimental findings and of polymers physical properties. However, the actual structures of the amorphous and crystalline regions of polymers are complex, and the fringed micelle model proved to be an oversimplification.

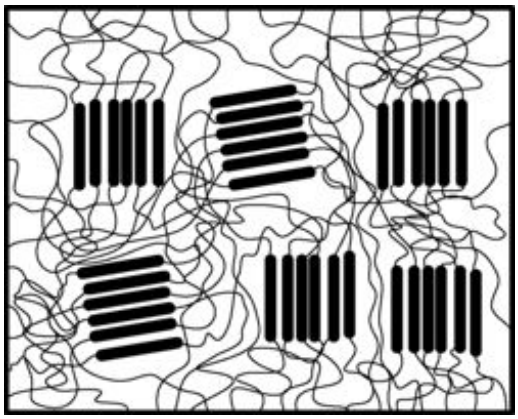

Fig. 4.2: representation of the fringed micelle model (Dargazany et al., 2014).

The discovery of polymer single crystals and the existence of supramolcular structures (spherulites) were the triggering events leading to re-examination and improvement of the fringed micelle model.

Due to the difficult complete crystallization caused by the long-chain character of macromolecules, single crystals of polymeric substances are seldom observed and hard to obtain. Sauter has first reported polyoxymethylene single crystal growth during polymerization (Sauter, 1932), but only during the 1950s, after crystal growth was observed from solution by cooling (Fischer, 1957; Keller, 1957; Till, 1957), the existence of polymer single crystals was generally recognized. Since these studies, the lamellar crystal habit has been shown to be the more frequent for most polymers, leading to various lamellar models (examples shown in Fig. 4.3) that will not be discussed here in detail.

The main innovation introduced by the lamellar models is the recognition of the fibrous-lamellar nature of the polymer crystallites (Hearle, 1963) and the statement that chains are aligned along the shortest extension of the *lamellae*. The polymer chains fold back and forth along layers, and the lamellar thickness is determinate by the length of the folds (Keller, 1959, 1957).

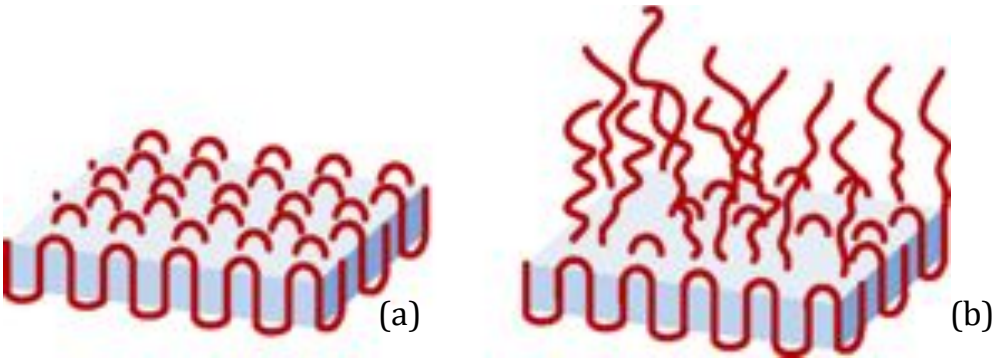

Fig. 4.3: schematic view of a lamella in the (a) adjacent re-entry and (b) switchboard models (Dargazany et al., 2014).

The second reason for the inaccuracy of the fringed micelle model, was the evidence of large crystalline superstructures characterized by spherical symmetry (Geil, 1963). These spherical aggregates, called *spherulites*, can be recognized by their typical appearance when observed in polarized microscope between crossed polarizers (see Fig. 4.4), showing a characteristic Maltese cross.

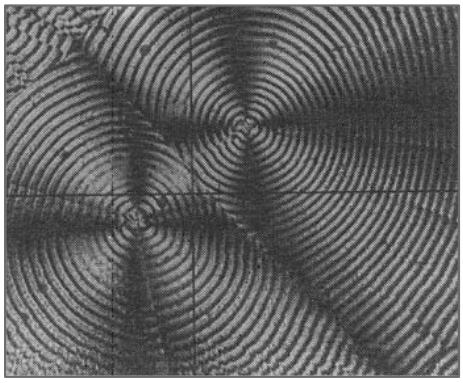

Fig. 4.4: Spherulites observed in a polarizing microscope micrograph under crossed polarizers (200x) (Keller, 1992).

These kinds of structures are the product of the crystalline fibrils aggregation, growing radially from a primary nucleus at the center (Hill, 1953), as shown in Fig. 4.5. Spherulitic growth and spherulites morphology has been extensively studied (Hill, 1953; Keller, 1959): since it was observed in a great variety of crystallizable polymers, spherulitic structure is considered to be the universal mode of crystallization. However, more recent studies (Mandelkern et al., 1981; Maxfield and Mandelkern, 1977) have shown that spherulitic structures are not always found, and that different supramolecular structures exist. The forming supramolecular structure depends on molecular weight, crystallization conditions and structural regularity of the molecule.

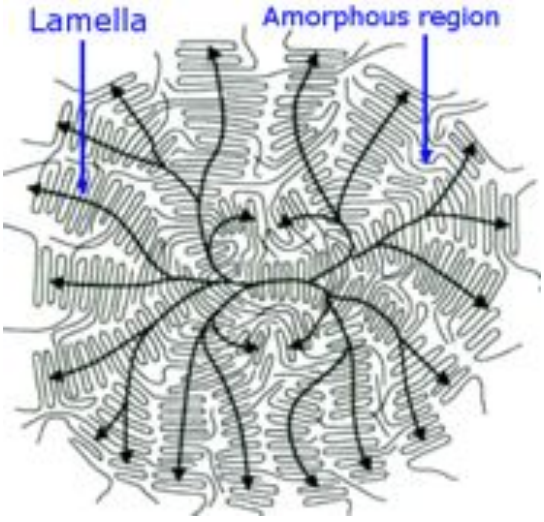

Fig. 4.5: Schematic representation of a spherulite ("Spherulite (polymer physics)," 2014).

4.2 Crystallization from solution, from the melt and through orientation

Different structures arise if polymer crystallization occurs from a dilute solution, a concentrated solution, the melt, or under an applied stress.

Generally, linear polymers form a variety of single crystals when they are crystallized from very dilute solutions upon cooling. For an increased polymer concentration a precipitate of lammellar aggregates will be observed, while further concentration leads up to more complex structures (twins, spirals, dendritic multilayer structures, etc.). At the highest concentrations, or when polymers crystallize from the melt, spherulites are the most common structure (Carraher, 2003; Keller, 1992) (see *Chapter 2*, Fig. 2.6).

If the formed crystallites are subject to an applied stress, orientation of the *lamellae* may result in the so-called *shish-kebab* arrangement. The shish-kebab structures often organize into larger ones giving rise to bundles of filaments forming fibrils (Carraher, 2003).

4.3 Structural characteristics governing crystallization

Not all polymers are capable of crystallizing: Bunn reports in 1954 the molecular characteristics that determine weather a long-chain molecule will be able to crystallize (Bunn, 1954).

The most important criterion for polymer crystallizability is structural regularity of the molecule, that is, a regular chemical and sterochemical structure and the absence of geometrical isomers. Other important variables are chain length and polydispersity.

Typically, crystallizable polymers consist in homopolymers obtained through condensation polymerization (as polyesters and polyamides), or addition-type polymers with identical substituents on a given chain.

However, absolute regularity is not essential, a certain amount of chain irregularity can be tolerated, poly(vinyl chloride), poly(acylonnitrile) and poly(vinyl alcohol) are some examples of partially crystalline polymers despite the possible occurrence of stereochemical irregularity (Bunn, 1948; Mandelkern, 1956). The requirement in the case of geometrically irregular homopolymers and of crystallizable copolymers is that the different units must not be too different in size and shape (Bunn, 1954), so that an approximation to regularity is achieved.

Polymers with highly regular molecules that are non-capable to crystallize are very uncommon, if crystallization is not achieved, the substance may be difficult to crystallize and the right conditions may not have been found.

4.4 Crystalline-amorphous combinations

Ordered polymers are seldom 100% crystalline, exception made for polymer single crystals, but consist of a combination of crystalline and amorphous regions. Also within the ordered regions, e.g. in a spherulite, amorphous regions persist, due to amorphous chain segments getting trapped within the forming crystalline platelets (Carraher, 2003). The same molecule may have segments being part of a crystallite and segments passing through the amorphous regions: these chains act as tie molecules, providing inter-crystalline links that are responsible for the characteristic good toughness found in semi-crystalline polymers (Carraher, 2003). The crystalline platelets are thus responsible for polymers strength, but also for its brittleness.

Though, the characteristic crystalline-amorphous combination in semi-crystalline polymers is very important, because it permits to obtain materials that have both, good strength (thanks to crystalline regions) and flexibility or “softness” (derived from the amorphous regions).

4.5 Degree of crystallinity

As highlighted in section 4.4, the degree of crystallinity, that is, the fractional amount of crystallinity in the polymer sample (Allegra et al., 1989) has a direct relationship with the materials mechanical behavior. Also a large number of other properties, i.e. density, enthalpy of fusion, infrared absorption, wide- and small-angle x-ray scattering intensity, depend primarily on this parameter.

Several experimental techniques permit to determine the degree of crystallinity; the most commonly used are (i) density measurements, (ii) calorimetric methods, (iii) spectroscopic methods and (iv) X-ray analysis.

It is worth to note, that even the degree of crystallinity is demonstrated to be a quantitave concept, some disagreement among the results obtained by the different techniques is frequently observed, specially at low degrees of crystallinity (Mandelkern, 1956).

Methods used for determination of this parameter by means of the different techniques will be discussed more in detail in the experimental section (see chapter 7).

References

Allegra, G., Corradini, P., Elias, H.-G., Geil, P.H., Keith, H.D., Wunderlich, B., 1989. Definitions of terms relating to crystalline polymers. Pure Appl. Chem. 61, 769–785.

Bunn, C.W., 1948. Crystal structure of Polyvinyl Alcohol. Nature 161, 929–930.

Bunn, C.W., 1954. Molecular Structure and the Crystallinity of Long-Chain Polymers. J. Appl. Phys. 25, 820–825.

Carraher, C.E., 2003. Seymour/Carraher's Polymer Chemistry: Sixth Edition. CRC Press.

Dargazany, R., Khiêm, V.N., Poshtan, E.A., Itskov, M., 2014. Constitutive modeling of strain-induced crystallization in filled rubbers. Phys. Rev. E 89, 022604.

Fischer, E.W., 1957. Stufen- und spiralformiges Kristallwachstum bei Hochpolymern. Z. Für Naturforschung A 12, 753–754.

Flory, P.J., 1949. Thermodynamics of Crystallization in High Polymers. IV. A Theory of Crystalline States and Fusion in Polymers, Copolymers, and Their Mixtures with Diluents. J. Chem. Phys. 17, 223–240.

Geil, P.H., 1963. Polymer single crystals. Interscience Publishers.

Hearle, J.W.S., 1963. The fine structure of fibers and crystalline polymers. I. Fringed fibril structure. J. Appl. Polym. Sci. 7, 1175–1192.

Herman, K., Gerngross, O., Abitz, W., 1930. X-ray studies of the structure of gelatin micelles. Z. Für Phys. Chem. B 10, 371–394.

Hill, R., 1953. Fibers from Synthetic Polymers. Edited by R. Hill. Elsevier Publishing Co., Amsterdam.

Keller, A., 1957. A note on single crystals in polymers: Evidence for a folded chain configuration. Philos. Mag. 2, 1171–1175.

Keller, A., 1959. The morphology of crystalline polymers. Makromol. Chem. 34, 1–28.

Keller, A., 1992. Morphology of polymers. Pure Appl. Chem. 64, 193–204.

Krevelen, D.W. van, Nijenhuis, K., 2009. Properties of Polymers: Their Correlation with Chemical Structure; their Numerical Estimation and Prediction from Additive Group Contributions. Elsevier.

Mandelkern, L., 1956. The Crystallization Of Flexible Polymer Molecules. Chem. Rev. 56, 903–958.

Mandelkern, L., 2004. Crystallization of Polymers: Volume 2, Kinetics and Mechanisms. Cambridge University Press.

Mandelkern, L., Glotin, M., Benson, R.A., 1981. Supermolecular structure and thermodynamic properties of linear and branched polyethylenes under rapid crystallization conditions. Macromolecules 14, 22–34.

Mark, J., 2004. Physical Properties of Polymers. Cambridge University Press.

Maxfield, J., Mandelkern, L., 1977. Crystallinity, Supermolecular Structure, and Thermodynamic Properties of Linear Polyethylene Fractions. Macromolecules 10, 1141–1153.

Rice, S.A., 2004. Advances in Chemical Physics. John Wiley & Sons.

Sauter, E., 1932. Rongtenometrische Untersuchungen an hochmolekularen Polyoxymethylen. Z. Für Phys. Chem. B 18, 417–435.

Spherulite (polymer physics), 2014. . Wikipedia Free Encycl.

Till, P.H., 1957. The growth of single crystals of linear polyethylene. J. Polym. Sci. 24, 301–306.

Chapter 5 – Poly(vinyl alcohol) and its hydrogels

This chapter will introduce the properties of poly(vinyl alcohol) and some of the known methods to obtain its hydrogels. The mechanisms involved in sol-gel transitions and models for the resulting structures will also be presented. Swelling behavior of hydrogels containing crystallites and the polymers characteristics that affect crystallizability are briefly discussed and, finally, some of the most studied blended poly(vinyl alcohol) hydrogels are presented, with special attention to blends with poly(vinyl pyrrolidone) and poly(ethylene glycol).

5.1 Poly(vinyl alcohol) and its hydrogels

Poly(vinyl alcohol) (PVA) is a polymer of large interest, that has been used in a variety of fields because of its desirable characteristics for many different applications and its ease of processing. Thanks to its elastic and adhesive properties and its chemical stability it is widely used in the textile and paper industry (Kleber and Stuhler, 1983) and as an additive to enhance cement and mortar properties (Kim et al., 1999). Furthermore, low toxicity and high biocompatibility of PVA make it suitable for the synthesis of biomaterials for pharmaceutical and biomedical use: PVA based hydrogels are largely used as drug delivery systems and in tissue engineering (Hoffman, 2002).

As recalled in *Chapter 1*, peelable PVA/Borate hydrogels are also used for the cleaning of cultural heritage artifacts (Natali et al., 2011) (Carretti et al., 2010) (Carretti et al., 2009).

5.1.1 Structure and properties of PVA

PVA is a vinyl polymer with a structure characterized by pendant hydroxyl groups (Fig. 5.1). Unlike other vinyl polymers it is not synthetized through polymerization of his monomer: vinyl alcohol does not exist because it rearranges to its stable tautomer, acetaldehyde. PVA is therefore produced through hydrolysis of poly(vinyl acetate) (PVAc), obtained by polymerization of vinyl acetate.

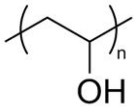

Fig. 5.1: chemical structure of poly(vinyl alcohol)

Since the hydrolysis reaction is not complete, PVA is in fact always a copolymer of PVA and PVAc. The hydrolysis degree (HD), or acetate groups content in the polymer, is one of the most important parameters, having a great influence on its chemical properties, in particular on solubility and crystallizability.

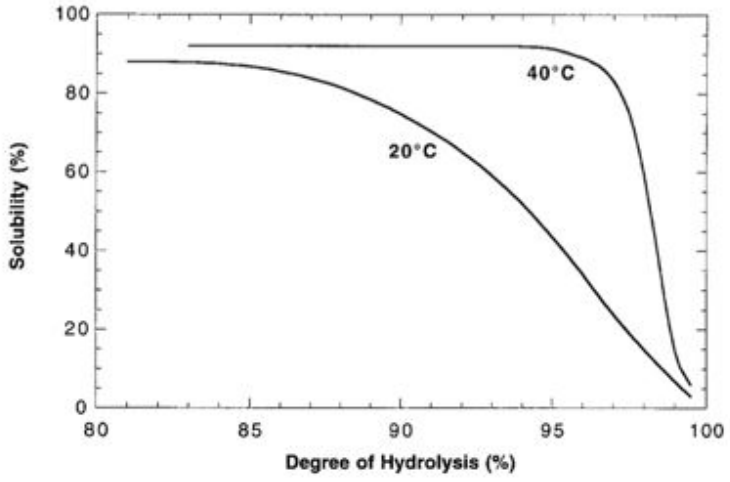

Fig. 5.2: Influence of hydrolysis degree on solubility of PVA at different temperatures (Hassan and Peppas, 2000).

Considering PVA samples with the same average molecular weight, it is shown that solubility in water increases for PVA with low degrees of hydrolysis (Fig. 5.2). The higher amount of residual acetate groups weakens inter- and intramolecular hydrogen bonding, favoring the dissolution process. Solubility is also function of temperature, so PVA with high hydrolysis degrees may be soluble by rising it over 90°C.

As in most polymers, molecular weight and molecular weight distribution strongly affect chemical properties. Commercial grades of PVA are generally available from 80% to full hydrolyzed (99+%), average molecular weights range from $M_w \approx$ 5000 to $M_w \approx$ 200,000, and polydispersity index of 2-2.5 are common.

PVA is a semi-crystalline polymer and its crystalline melting range is reported to be between 220°-240°C. As received, PVA is usually about 20-30% crystalline, but through annealing above its T_g crystallinity can reach up to 70% (Peppas, 1987). For dry PVA films T_g is reported to be 85°C, but a considerable decrease of glass transition temperature has been detected in the presence of water (Peppas and Merrill, 1976).

5.1.2 Synthesis of PVA based hydrogels

As already mentioned in *Chapter 1*, to form a gel a network is needed, hence, to obtain a hydrogel, PVA must be crosslinked. Synthesis methods to obtain hydrogels from PVA include both, chemical and physical crosslinking.

Chemically crosslinked PVA networks can be obtained through the use of difunctional crosslinking agents such as glutaraldehyde, acetaldehyde, fromaldehyde etc. In acid environment (e.g. sulfuric acid, acetic acid) or methanol, acetal bridges are formed between hydroxyl groups, resulting in a tridimensional network.

For applications in the biomedical field, undesirable toxic residues of crosslinking agents must be avoided. Thus, other chemical crosslinking methods, such as

electron beam or γ-irradiation of concentrated PVA solutions, were early developed (Danno, 1958; Peppas and Merrill, 1976).

The properties of partially crystalline PVA hydrogels, first chemically crosslinked through electron beam irradiation and afterwards subject to a process of dehydration and annealing, were firstly examined by Peppas and Merrill (Peppas and Merrill, 1977). In addition to the chemical crosslinks produced through irradiation of the aqueous PVA solution, the resulting materials contained also crystallites. These additional crosslinks, produced by the heat treatment, permit to enhance the hydrogels mechanical properties by redistributing external stresses along the crystallites (Peppas and Merrill, 1977).

Peppas investigated through a profuse work started in the early seventies, a second mechanism of PVA hydrogel formation that involves the sole physical crosslinking due to crystallites formation (Peppas, 1975). He reports the unusual characteristic of PVA to form crystallites upon repeated cycles of freezing and thawing. The resulting hydrogels exhibit higher mechanical strength than hydrogels obtained through conventional crosslinking methods, a high degree of swelling in water and a rubbery and elastic nature. Because of their physical properties, the biomedical appears to be the main field of interest: these new materials exhibit low toxicity, they contain no impurities and their water content matches that of tissue.

Further investigated methods to introduce physical crosslinks through crystallites formation in PVA hydrogels are crystallization through aging (Sone et al., 1953) and by means of slow-drying rate dehydration in isothermal conditions after chemical crosslinking with electron beam irradiation (Peppas, 1976).

More recently, a method to obtain physically crosslinked PVA hydrogels, without addition of further chemicals or irradiation is reported (Otsuka and Suzuki, 2009; Peppas and Tennenhouse, 2004). In these studies, PVA-water solutions are casted and dried at room temperature: after dehydration gels swell, but do not solubilize in water at room temperature.

The following section focuses on the general behavior of PVA/water systems during sol-gel transitions, with a more deep insight on the mechanisms involved in

gel formation when the systems are subject to repeated freezing and thawing cycles (freeze-thawing method) or to simple slow dehydration (cast-drying method).

5.2 Sol-gel transitions in PVA-water systems

As described in *Chapter 3*, sol-gel transitions may occur according to different mechanisms most of them being related to liquid-liquid phase separation, polymer crystallization, or strong association of the polymer chains.

PVA-water systems are known to form thermoreversible gels, that is, fluidity of the solution is lost during cooling and recovered upon heating. Kawanishi et al. discuss possible gelation mechanism and their relation to the nature of network tie-points that form during gelation, through the analysis of phase diagrams obtained from light scattering experiments on PVA-water systems (Kawanishi et al., 1987).

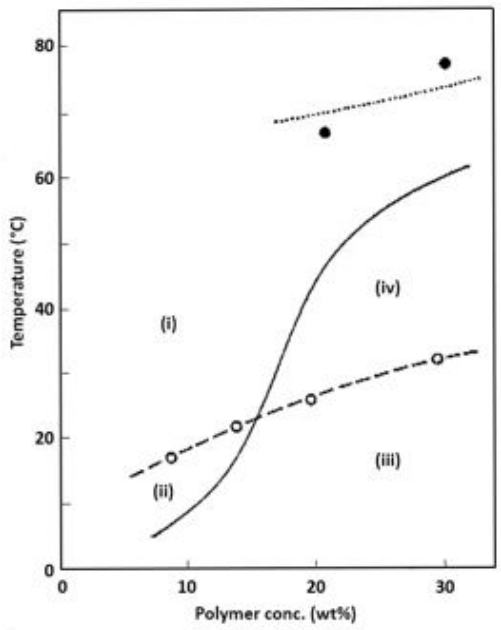

Fig. 5.3: Phase diagram for a PVA (M_n=500)/water system. Sol-gel transition (continuous line), spinodal (dashed line) and gel-melting curves (dotted line) are shown (Kawanishi et al., 1987). It is worth to remark that phase diagram regions strongly depend on polymer molecular weight.

PVA/water systems display an upper critical solution temperature (UCST) and, within the phase diagram, four different regions are identified (see Fig. 5.3):

i) The solution is a *sol*;

ii) Phase separation trough liquid-liquid demix occurs, but no gel is formed;

iii) Both, gelation and liquid-liquid demix occur,

iv) Gelation takes place without liquid-liquid demix.

Moreover, in regions (iii) and (iv), broad X-ray diffraction peaks are observed after a gelation time of at least 20 hours, indicating that liquid-solid phase separation takes place in the late stages of gelation.

Basing on these observations, Kawanishi states that in PVA/water systems, liquid-liquid demix is weather a necessary, nor a sufficient condition to achieve sol-gel transition. Gelation appears to be very complex, manly due to partial or total sequential superposition of three fundamental events: H-bonding type association, crystallite formation (solid-liquid demix) and liquid-liquid phase separation. According to the different regions identified in the phase diagram, different gelation processes are proposed.

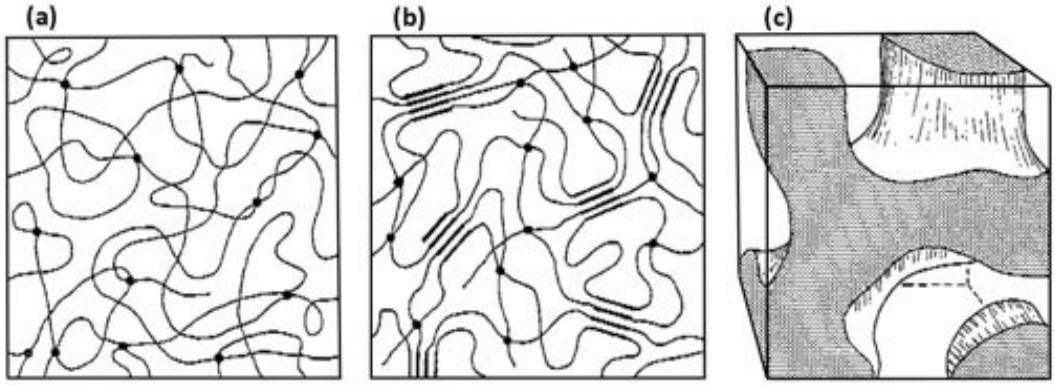

Fig. 5.4: schematic representation of (a) a network formed by hydrogen bonding, (b) a solvent swelled network formed by crystallites and (c) a network formed through liquid-liquid demixing (Kawanishi et al., 1987).

In region (iv), gelification in the early stages occurs through hydrogen-bonding type association (Fig. 5.4a), later chains organize into crystallites, forming a solvent

swollen network (see Fig. 5.4b).

In region (iii), where liquid-liquid demixing is observed, an interconnected structure of polymer-rich and polymer-poor regions is formed (as in Fig. 5.4c). Demixing is a fast process, followed by gelation within the polymer-rich regions during the ensuing stages. Gelation then probably occurs according to the same mechanism as in region (iv), i.e. first through hydrogen bonding, followed by crystallites formation.

In region (ii), although liquid-liquid demix occurs, the failing in gel formation is due to interruption of interconnectivity of the polymer-rich phase, resulting in isolated polymer-rich droplets. On the other hand, in region (i) gel formation does not occur because the probability of hydrogen-bond association is too low to form an infinite network. Even possible crystallites forming in the very late stages may be isolated and, thus, cannot act as tie-points of the network.

The described process explains the behavior of a simple PVA solution standing at room temperature, consisting in the most conventional method to obtain a thermoreversible, physically cross-linked PVA hydrogel. However, as already mentioned in the previous sections, PVA/water solutions are able to form hydrogels also upon repeated freezing and thawing cycles. In respect to the former hydrogels, PVA hydrogels produced through repeated freezing and thawing cycles display a dramatic decrease in tackiness, an increase in water-resistance and an elastic modulus orders of magnitude larger (Peppas and Stauffer, 1991; Yokoyama et al., 1986). It seems that PVA is a unique polymer showing rubber-elasticity after its hydrogel is prepared through freezing (Yokoyama et al., 1986).

Peppas and Yokoyama propose the first gelation models for these systems, postulating a micro-phase separate structure formed during freezing, with segregation into a polymer-rich and a polymer-poor phase, in which freezing occurs in the polymer-poor phase (i.e. the ice crystal phase). The repeated crystallization of the polymer-poor phase consists in a refinement process for the ice crystals: whenever the system is frozen, polymer chains are rejected as an impurity. This process implies that by increasing the freezing cycle number, the PVA

concentration in the polymer-rich phase will be increased, while PVA concentration in the polymer-poor phase will be decreased. As the water freezes, molecular motion of PVA segments ceases, growing ice crystals force polymer chains to approach and hydrogen bonds between PVA hydroxyl groups are formed (see Fig. 5.5a and 5.5b). During the first cycle only a loose crosslinking network is formed and porosity is almost absent. The more the polymer-poor phase approaches pure water thanks to repeated segregation; the more evident becomes the porous structure of the gel (see Fig. 5.5c). This process is confirmed by SEM micrographs obtained by Hatekayama, revealing hydrogels with clearer and thicker cell walls with increasing freezing cycles (Hatakeyema et al., 2005).

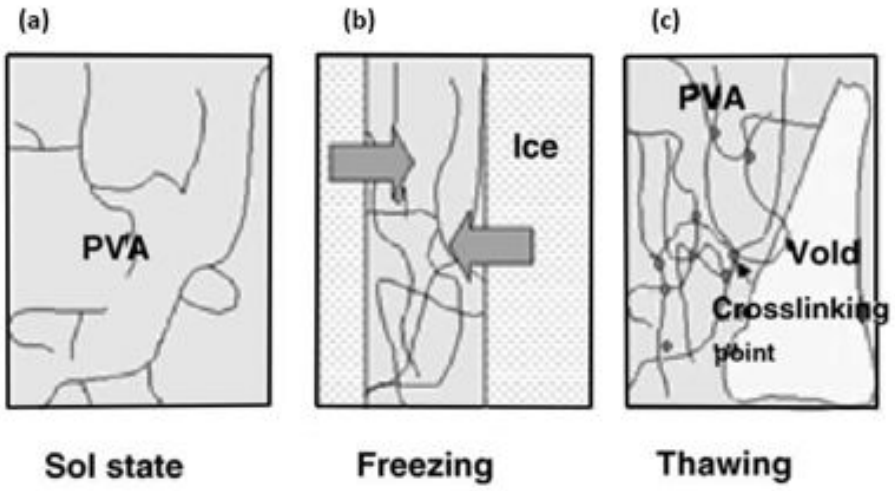

Fig. 5.5: Schematic representation of gel formation through freezing and thawing (Hatakeyema et al., 2005).

Crystallites, acting as junction points of the network, are formed within the polymer-rich segregated phase, contributing to strong enhancement of gelation. The presence of crystallites is confirmed by X-ray imges (Yokoyama et al., 1986), while the positive dependence of the dynamic modulus E' (Watase et al., 1983), is considered to reflect a rubber-like structure in which flexible amorphous chains are physically cross-linked by the rigid crystallites.

The number of freezing and thawing cycles has great influence on crystallinity of PVA hydrogels. X-ray diffraction data obtained by Ricciardi et al. confirm that

crystallinity degree is increased by increasing freezing cycles, mainly due to increase of the crystallites size, although formation of new crystalline aggregates can not be excluded (Ricciardi et al., 2004).

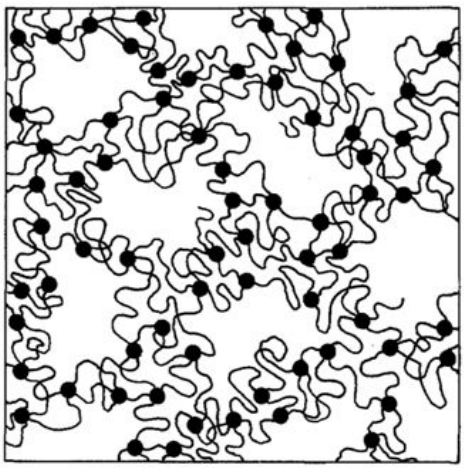

Fig 5.6: Structural model for a PVA-hydrogel obtained through repeated freezing and thawing. Solid circles represent PVA crystallites (Yokoyama et al., 1986).

The combination of these observation leads to the structural model shown in Fig. 5.6 where the hydrogel is composed of three phases: a water phase (or phase with a very low polymer concentration) corresponding to the ice crystal phase in the frozen gel, an amorphous phase in which every chain is associated with water, and a PVA crystal phase, that restrains mobility of the amorphous chains.

Crystallites formation is involved also in case of PVA hydrogels obtained through slow dehydration. Gelation and crystallization processes of PVA-water systems subject to controlled evaporation of the solvent were studied by Peppas and by Packter and Nerukar (Packter and Nerurkar, 1968; Peppas, 1976). Their results suggest that gelation occurs thanks to increase in polymer concentration during water evaporation. In the concentrated polymer solution, the strong inter-chain interactions lead to formation of three-dimensional networks (gelation), where the junction points may act as nuclei for eventual crystallization. After sol-gel transition, further increase of polymer concentration due to evaporation of the solvent leads to gel-glass transition of the system. Investigations on the

crystallization rates performed by Packter and Nerukar show that crystallization occurs within the range delimited by the gel-transition temperature T_{gel} and the glass transition temperature T_{glass}. T_{gel} and T_{glass} for different polymer weight fractions are presented in Fig. 5.7. At any temperature of evaporation, significant nucleation occurs when polymer weight fraction x_p reaches the sol-gel transition gap, while simultaneous nucleation and growth occurs until the composition for gel-glass transition is reached.

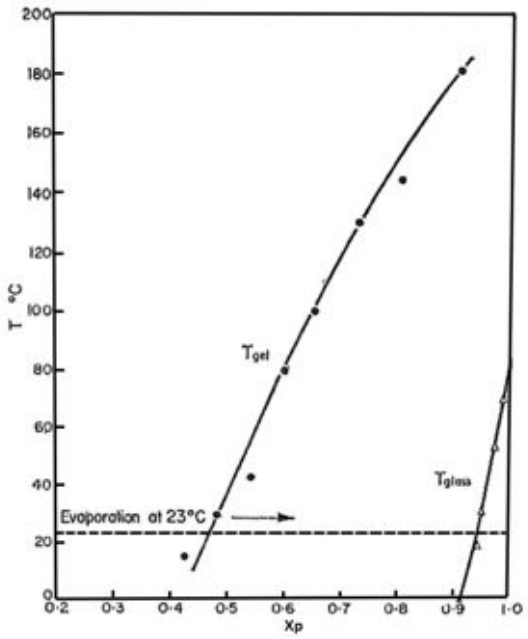

Fig. 5.7: Sol-gel and gel-glass transition temperatures for different PVA weight fractions in water (Packter and Nerurkar, 1968).

The rate of crystallization is initially low, rapid crystallization occurs well beyond the sol-gel transition composition, usually at $x_p \approx 0.7$, when the surface area of the crystalline regions is sufficiently high to promote crystal growth. When the glass-transition composition is reached, polymer chain mobility is strongly reduced and, thus, the crystallization rate becomes very low.

Despite the high degrees of crystallinity detected for the systems studied by Packter and Nerukar, microscopic examination did not permit to resolve crystalline regions suggesting a very small average crystallite size (below 0,1 μm) and a very large number of nuclei.

5.3 Characteristics that affect PVA crystallization ability

It is important to not confuse the gel formation process with crystallization. Polymer crystals may be formed although no gel is formed, and amorphous gels can be obtained.

As other crystallizable polymers, PVA can crystallize as single crystals or as lamellar or spherulitic aggregates. Single PVA crystals were first obtained by Tsuboi through isothermal crystallization from solution (Tsuboi and Mochizuki, 1963). Resulting crystals belong to the monoclinic system and the unit cell consists of two monomeric units. Lamellar thickness was estimated around 100-150 Å.

Packter and Nerurkar observed spherulitic crystal growth starting from concentrated PVA solutions in polyols (Packter and Nerurkar, 1969), while amorphous PVA films were obtained trough freeze-drying of isotactic PVA (Iohara et al., 1968).

In fact, tacticity has great influence on crystallizability of PVA. Fuji extensively studied crystallizability of PVA in relation to its stereoregularity (Fujii, 1971), finding that it is the sole polymer in which the atactic form is readily crystallizable. Furthermore, increasing stereoregularity decreases crystallizability, being the atactic form the more and the isotactic the less crystallizable form.

As stated by Bunn (Bunn, 1948) in discussing the crystalline structure of PVA, lateral hydroxyl groups on polymer chains represent no steric hindrance, since they are small enough to be interchangeable with hydrogen atoms within the crystalline lattice. However, the isotactic structure promotes intermolecular hydrogen bonding while the atactic form promotes intramolecular hydrogen bonding and, thus, favors crystalline orientation of the chains.

Another characteristic affecting PVA crystallizability is the hydrolysis degree. The presence of residual acetate groups weakens intra- and intermolecular hydrogen bonding, resulting in more difficult crystallization (Hassan and Peppas, 2000). Furthermore, usually a minimum chain length is necessary for PVA to crystallize, it has been reported that crystallites size increases as molecular weight increases (Mandelkern, 1967).

5.4 Swelling behavior

Once crystallites are formed, the polymer is able to swell in an appropriate liquid (e.g. water) without undergo solubilization. A generally accepted hypothesis, proved also by experimental data (Peppas, 1977), is that only the amorphous regions interact and are penetrated by the liquid molecules. The crystalline regions are able to act as cross-links, basically because they remain unaffected by the liquid. Swelling process consists mainly in the expansion of chain molecules of the non-crystalline region, due to interaction with the swelling agent, leading to volume increase of the polymer as a whole. During swelling, the force resisting to the expansion of the chains increases until swelling equilibrium is reached (Peppas, 1987). Considerable amounts of the amorphous regions may dissolve during swelling, but it has been proved that crystallinity is not changed (Sakurada et al., 1955). However, the presence of water in swelled hydrogels prevents further crystallization of PVA (Auriemma et al., 2008).

5.5 Blended PVA hydrogels

There is a considerable amount of research involved in the investigation PVA blended hydrogels. Some of the most studied hydrogels based on PVA polymer blends will be recalled, with special attention to the properties of PVA hydrogels obtained through blending with poly(vinyl pyrrolidone) (PVP) or poly(ethylene glycol) (PEG), since they are the topic of the present work. This section claims not to be complete; the aim is to illustrate how the addition of other polymers into PVA hydrogel structure permits to enhance specific characteristics to create materials with the desired properties; thus, some examples are presented.

Since pure PVA hydrogels are insensitive to pH changes, poly(acrylic acid) (PAA) is used to attain environmental-responsive PVA/PAA composite membranes with

increased permeselectivity for biochemical and biomedical separation. PVA/PAA composites can be prepared via conventional or freezing and thawing techniques. Gudeman and Peppas obtained PVA/PAA interpenetrating networks (IPNs), using glutaraldehyde as a cross-linking agent, and studied the gel response to changes in the pH and ionic strength of the swelling medium (Gudeman and Peppas, 1995a, 1995b).

In order to avoid potentially toxic residues (initiators, cross-linking agents, etc.), freeze-thawing technique is used for the preparation of physically cross-linked composite PVA/PAA membranes; since they exhibit size exclusion properties, Hickey and Peppas analyze solute transport within the membranes (Hickey and Peppas, 1997).

Biodegradable materials are obtained by blending PVA with biopolymers such as cellulose or its derivatives and proteins.

Membranes with improved strength and permeability, and with increased antibacterial activity, were obtained through blending chitosan and PVA. Blends are obtained using formaldehyde as a cross-linking agent (Yang et al., 2004), or through simple air drying of the solution (Chandy and Sharma, 1992). Physically and chemically cross-linked PVA/cellulose hydrogels with enhanced mechanical properties and high water uptakes were also prepared and characterized (Chang et al., 2008).

Blended hydrogels that could be used as a material for artificial skin were prepared by esterification of PVA with gelatin (Pawde and Deshmukh, 2008).

Studies on properties of PVA/PVP blended hydrogels report the preparation of physically cross-linked (by freeze-thawing or casting method) (Bernal et al., 2011; Cassu and Felisberti, 1997; Ma et al., 2009; Seabra and de Oliveira, 2004) or chemically cross-linked PVA/PVP polymer blends (Nishio et al., 1990). Blending PVA and PVP mainly affects mechanical properties and water content of the resulting hydrogels.

Experimental results show an increase in tensile strength for small amounts of

added PVP (1-5%), while high PVP contents result in hydrogels that are less resistant to elongation in respect to pure PVA films (Ma et al., 2009; Seabra and de Oliveira, 2004). PVP usually permits to increase equilibrium swelling and equilibrium water-content (Bernal et al., 2011; Ma et al., 2009). In respect to high molecular PVP, low molecular weight PVP promotes crystallization of PVA (Cassu and Felisberti, 1997).

Reported studies on miscibility between the two polymers show that blends display only one T_g and, thus, the systems proves to be miscible (Cassu and Felisberti, 1997; Seabra and de Oliveira, 2004). Variations on T_g are dependent on blends compositions and intimate intermolecular interactions between components are suggested by the systematic melting-point depression of PVA (Nishio et al., 1990).

Peppas and Tennenhouse, prepared PVA/PEG blended films through annealing of amorphous mixtures of the two polymers at temperatures higher than T_g, to permit crystallization of the macromolecules (Peppas and Tennenhouse, 2004). Resulting films were opaque, and DSC studies show that co-crystallization of the polymers occurred. Studies on long-term stability of the films confirm that co-crystallization of PEG stabilizes the polymer network.

Inamura et al. studied extensively the miscibility of ternary PVA-PEG-water systems, finding that miscibility is correlated to PEG molecular weight and that water is a better solvent for PEG than for PVA at polymer concentration where phase separation occurs (Inamura, 1986; Inamura et al., 1997, 1984).

References

Auriemma, F., De Rosa, C., Ricciardi, R., Lo Celso, F., Triolo, R., Pipich, V., 2008. Time-resolving analysis of cryotropic gelation of water/poly(vinyl alcohol) solutions via small-angle neutron scattering. J. Phys. Chem. B 112, 816–823.

Bernal, A., Kuritka, I., Saha, P., 2011. Poly (vinyl alcohol)-poly (vinyl pyrrolidone) blends: preparation and characterization for a prospective medical application. Presented at the Proceedings of the 13th WSEAS international conference on Mathematical and computational methods in science and engineering, World Scientific and Engineering Academy and Society (WSEAS), pp. 431–434.

Bunn, C.W., 1948. Crystal structure of Polyvinyl Alcohol. Nature 161, 929–930.

Carretti, E., Bonini, M., Dei, L., Berrie, B.H., Angelova, L.V., Baglioni, P., Weiss, R.G., 2010. New Frontiers in Materials Science for Art Conservation: Responsive Gels and Beyond. Acc Chem Res 43, 751–760.

Carretti, E., Grassi, S., Cossalter, M., Natali, I., Caminati, G., Weiss, R.G., Baglioni, P., Dei, L., 2009. Poly(vinyl alcohol)−Borate Hydro/Cosolvent Gels: Viscoelastic Properties, Solubilizing Power, and Application to Art Conservation. Langmuir 25, 8656–8662.

Cassu, S.N., Felisberti, M.I., 1997. Poly(vinyl alcohol) and poly(vinyl pyrrolidone) blends: miscibility, microheterogeneity and free volume change. Polymer 38, 3907–3911.

Chandy, T., Sharma, C.P., 1992. Prostaglandin E1-immobilized poly(vinyl alcohol)-blended chitosan membranes: Blood compatibility and permeability properties. J. Appl. Polym. Sci. 44, 2145–2156.

Chang, C., Lue, A., Zhang, L., 2008. Effects of Crosslinking Methods on Structure and Properties of Cellulose/PVA Hydrogels. Macromol. Chem. Phys. 209, 1266–1273.

Danno, A., 1958. Gel Formation of Aqueous Solution of Polyvinyl Alcohol Irradiated by Gamma Rays from Cobalt-60. J. Phys. Soc. Jpn. 13, 722–727.

Fujii, K., 1971. Stereochemistry of poly(vinyl alcohol). J. Polym. Sci. Macromol. Rev. 5, 431–540.

Gudeman, L.F., Peppas, N.A., 1995a. pH-sensitive membranes from poly(vinyl alcohol)/poly(acrylic acid) interpenetrating networks. J. Membr. Sci. 107, 239–248.

Gudeman, L.F., Peppas, N.A., 1995b. Preparation and characterization of pH-sensitive, interpenetrating networks of poly(vinyl alcohol) and poly(acrylic acid). J. Appl. Polym. Sci. 55, 919–928.

Hassan, C.M., Peppas, N.A., 2000. Structure and Applications of Poly(vinyl alcohol) Hydrogels Produced by Conventional Crosslinking or by Freezing/Thawing Methods, in: Biopolymers · PVA Hydrogels, Anionic Polymerisation Nanocomposites, Advances in Polymer Science. Springer Berlin Heidelberg, pp. 37–65.

Hatakeyema, T., Uno, J., Yamada, C., Kishi, A., Hatakeyama, H., 2005. Gel–sol transition of poly(vinyl alcohol) hydrogels formed by freezing and thawing. Thermochim. Acta, A collection of papers from the 40th Anniversary Japanese Conference on Calorimetry and Thermal Analysis held in Tokyo, Japan, October 12 - 14, 2004 431, 144–148.

Hickey, A.S., Peppas, N.A., 1997. Solute diffusion in poly(vinyl alcohol)/poly(acrylic acid) composite membranes prepared by freezing/thawing techniques. Polymer 38, 5931–5936.

Hoffman, A.S., 2002. Hydrogels for biomedical applications. Adv. Drug Deliv. Rev., Recent Developments in Hydrogels 54, 3–12.

Inamura, I., 1986. Liquid-Liquid Phase Separation and Gelation in the Poly(vinyl alcohol)-Poly(ethylene glycol)–Water System. Dependence on Molecular Weight of Poly(ethylene glycol). Polym. J. 18, 269–272.

Inamura, I., Akiyama, K., Kubo, Y., 1997. Polymer 2-Polymer 3 Interactions in Water 1/Polymer 2/Polymer 3 Ternary Systems. Polym. J. 29, 119–122.

Inamura, I., Toki, K., Tamae, T., Araki, T., 1984. Effects of Molecular Weight on the Phase Equilibrium of a Poly(vinyl alcohol)–Poly(ethylene glycol)–Water System. Polym. J. 16, 657–660.

Iohara, K., Suehiro, K., Kilmada, K., Takayanagi, M., 1968. PVA in amorphous state prepared by freeze-drying method. Rep. Prog. Polym. Phys. Jpn. 11, 207.

Kawanishi, K., Komatsu, M., Inoue, T., 1987. Thermodynamic consideration of the sol-gel transition in polymer solutions. Polymer 28, 980–984.

Kim, J.-H., Robertson, R.E., Naaman, A.E., 1999. Structure and properties of poly(vinyl alcohol)-modified mortar and concrete. Cem. Concr. Res. 29, 407–415.

Kleber, R., Stuhler, H., 1983. Sizing agent for synthetic fibers. Google Patents.

Mandelkern, L., 1967. The effect of molecular weight on the crystallization and melting of long-chain molecules. J. Polym. Sci. Part C Polym. Symp. 18, 51–55.

Ma, R., Xiong, D., Miao, F., Zhang, J., Peng, Y., 2009. Novel PVP/PVA hydrogels for articular cartilage replacement. Mater. Sci. Eng. C 29, 1979–1983.

Natali, I., Carretti, E., Angelova, L., Baglioni, P., Weiss, R.G., Dei, L., 2011. Structural and Mechanical Properties of “Peelable” Organoaqueous Dispersions with Partially Hydrolyzed Poly(vinyl acetate)-Borate Networks: Applications to Cleaning Painted Surfaces. Langmuir 27, 13226–13235.

Nishio, Y., Haratani, T., Takahashi, T., 1990. Miscibility and orientation behavior of poly(vinyl alcohol) / poly(vinyl pyrrolidone) blends. J. Polym. Sci. Part B Polym. Phys. 28, 355–376.

Otsuka, E., Suzuki, A., 2009. A simple method to obtain a swollen PVA gel crosslinked by hydrogen bonds. J. Appl. Polym. Sci. 114, 10–16.

Packter, A., Nerurkar, M.S., 1968. Crystallization in films of polar vinyl polymers—I. Crystallinity of polyvinyl alcohol films prepared by evaporation of aqueous solutions. Eur. Polym. J. 4, 685–693.

Packter, A., Nerurkar, M.S., 1969. Spherulitic polyvinyl alcohol films from concentrated polyol solutions. J. Polym. Sci. [B] 7, 761–764.

Pawde, S.M., Deshmukh, K., 2008. Characterization of polyvinyl alcohol/gelatin blend hydrogel films for biomedical applications. J. Appl. Polym. Sci. 109, 3431–3437.

Peppas, N.A., 1975. Turbidimetric studies of aqueous poly(vinyl alcohol) solutions. Makromol. Chem. 176, 3433–3440.

Peppas, N.A., 1976. Crystallization of polyvinyl alcohol-water films by slow dehydration. Eur. Polym. J. 12, 495–498.

Peppas, N.A., 1977. Infrared spectroscopy of semicrystalline poly(vinyl alcohol) networks. Makromol. Chem. 178, 595–601.

Peppas, N.A., 1987. Hydrogels of poly(vinyl alcohol) and its coplymers, in: Hydrogels in Medicine and Pharmacy. CRC Press, Boca Raton, FL, pp. 1–48.

Peppas, N.A., Merrill, E.W., 1976. Differential Scanning Calorimetry of Crystallized PVA Hydrogels. J. Appl. Polym. Sci. 20, 1457–1465.

Peppas, N.A., Merrill, E.W., 1977. Development of semicrystalline poly(vinyl alcohol) hydrogels for biomedical applications. J. Biomed. Mater. Res. 11, 423–434.

Peppas, N.A., Stauffer, S.R., 1991. Reinforced uncrosslinked poly (vinyl alcohol) gels produced by cyclic freezing-thawing processes: a short review. J. Controlled Release 16, 305–310.

Peppas, N.A., Tennenhouse, D., 2004. Semicrystalline poly(vinyl alcohol) films and their blends with poly(acrylic acid) and poly(ethylene glycol) for drug delivery applications. J. Drug Deliv. Sci. Technol. 14, 291–297.

Ricciardi, R., Auriemma, F., De Rosa, C., Lauprêtre, F., 2004. X-ray Diffraction Analysis of Poly(vinyl alcohol) Hydrogels, Obtained by Freezing and Thawing Techniques. Macromolecules 37, 1921–1927.

Sakurada, I., Nukushima, Y., Sone, Y., 1955. Behavior of crystalline regions in swelling. Kobunshi Kagaku 12, 510.

Seabra, A.B., de Oliveira, M.G., 2004. Poly(vinyl alcohol) and poly(vinyl pyrrolidone) blended films for local nitric oxide release. Biomaterials 25, 3773–3782.

Sone, Y., Hirabayashi, K., Sakurada, I., 1953. Variation in the Degree of Swelling in Water and Hot Water Resistance of Gel by Aging. Kobunshi Kagaku Chem High Polym. 10, 1–7.

Tsuboi, K., Mochizuki, T., 1963. Single crystals of polyvinyl alcohol. J. Polym. Sci. [B] 1, 531–534.

Watase, M., Nishinari, K., Nambu, M., 1983. Rheological properties of an anomalous poly (vinyl alcohol) gel. Polym. Commun. 24, 52–54.

Yang, J.M., Su, W.Y., Leu, T.L., Yang, M.C., 2004. Evaluation of chitosan/PVA blended hydrogel membranes. J. Membr. Sci. 236, 39–51.

Yokoyama, F., Masada, I., Shimamura, K., Ikawa, T., Monobe, K., 1986. Morphology and structure of highly elastic poly(vinyl alcohol) hydrogel prepared by repeated freezing-and-melting. Colloid Polym. Sci. 264, 595–601.

Part III

Experimental

Chapter 6 – Hydrogel preparation

The present chapter illustrates the preparation procedures and the materials used for the synthesis of the characterized hydrogel systems.

6.1 Hydrogel preparation

Hydrogel formulations were synthesized according to two different methods: cast-drying (cast-drying method) and repeated freezing and thawing cycles (freeze-thawing method). Different hydrogel formulations were prepared to understand the role of different components in final properties. Hydrogels were obtained starting from pure PVA-water solutions, but also through blended systems obtained by addiction of poly(vinylpyrrolidone) (PVP) and poly(ethylene glycol) (PEG) to the solutions. Blended components were added to investigate their influence on mechanical properties such as softness and adhesion, but also to tune hydrogels hydrophylicity.

6.1.1 Method

Both synthesis methods (cast-drying and freeze-thawing) lead to formation of physically cross-linked PVA based hydrogels. Gelification is obtained by exploiting the ability of this polymer to form crystallites that act as junction points within the hydrogel network.

During both processes, cast-drying and freeze-thawing, gel formation occurs due to a restriction in molecular motion that implies an increase in molecular interactions, that is hydrogen bonds, between neighboring chains. Restriction in molecular

motion induced by both, cooling of the homogeneous solution (freeze-thawing) and solvent evaporation (cast-drying), permits the formation of small crystalline nuclei. Induced crystallites formation, that is, the formation of a physically cross-linked network, was carried out on pure PVA aqueous solution or on solutions obtained by adding a second linear polymer (PVP or PEG). In this latter case, depending on composition and synthesis conditions a homogenous or a 2-phase system is formed. The crystallization process of PVA is influenced also by heat treatments at temperatures above the T_g (annealing). Heating at temperatures over the T_g promotes chain mobility and permits structural reorganization, i.e. nucleation or growth of already existing crystallites. Thus, after cast-drying, some preparation were subject to annealing to investigate how hydrogel structure is affected by heat treatment. Annealing conditions were 4h at 120°C.

6.1.2 Materials

Table 6.1 lists the chemicals used for hydrogel preparation. All chemicals were used as received. Water used for the preparation of polymer solutions was purified by a Millipore MilliRO-6 Milli-Q gradient system (resistivity >18 MΩ). To favor solubilization, before use PVA 98-99% HD was hydrated in water for at least 12 hours.

Chemical	Company	av. Mw (g/mol)	HD (%)
Polyvinylalcohol	Sigma-Aldrich	146,000-186,000	98-99
Polyvinylalcohol	Sigma-Aldrich	85,000-124,000	87-89
Polyvinylpirrolidone	Sigma-Aldrich	40,000	-
Polyvinylpirrolidone	Sigma-Aldrich	1300000	-
Polyethyleneglycol	Fluka	35,000	-

Table 6.1: Chemicals used for hydrogel preparation.

6.1.3 Preparation procedure

Aqueous polymer solutions were obtained by dissolving the weighted quantity of PVA powder into purified water at 90°C for 2h under magnetic stirring in a double neck flask equipped with a condenser to avoid water evaporation during heating. After complete dissolution of PVA, the second component (PVP or PEG) is added and the solution is stirred at 80°C for 4h to achieve complete homogenization. To obtain a transparent solution, gas bubbles due to stirring are removed through 15 minutes sonication in pulsed mode. Weight fractions of the different components within the prepared solutions are provided in Table 8.1, Chapter 8, section 8.1.

Cast-drying method

Polymer solutions (7,5g) are casted into a petri dish with an inner diameter of 50mm and dried for 12h at 50°C under nitrogen flow. Obtained xerogels are extremely transparent and hard and can be rehydrated by adding deionized water into the petri dish. After washing, films can be stored in water-filled falcons.
Before rehydration some formulations were subject to annealing for 4h at 120°C.

Freeze-thawing method

Polymer solutions are poured in two different kind of molds: 50mm diameter petri dishes (7,5g polymer solution) to obtain hydrogels in film form or plastic molds that permit to obtain parallelepiped shaped hydrogels with dimensions of approximately 2,5 × 2,5 × 1 cm.
The molds are covered with a lid and sealed with Parafilm® to prevent evaporation during the thawing cycles. Solutions are subject to repeated freezing (8h at -23°C) and thawing cycles (16h at room temperature). After gelification hydrogels are washed and stored into falcons filled with deionized water.

Chapter 7 – Hydrogel characterization: methods and instrumental conditions

This chapter provides equations and instrumental conditions used for the investigation of some representative parameters and for the structural characterization of the prepared hydrogel systems.

7.1 Gel fraction

Evaluation of the insoluble fraction of the gel was performed to evaluate the efficiency of gel formation, that is, the efficiency of crosslinking through crystallites formation between PVA chains, and of embedding the water-soluble PVP chains.

After synthesis gels are stored in deionized water for at least 7 days to permit the extraction of the still water-soluble components. Water is changed every 24 hours to ensure complete removal of the solubilized materials.
After extraction of the water-soluble components, the gel fraction is determined gravimetrically through the formula

$$G\ (\%) = (W_d/W_0) \times 100 \qquad \text{(Eq. 7.1)}$$

Where W_0 is dry weight of the sample with residual soluble components (not extracted), while W_d is the dry weight after extraction of soluble components. Dry weights are determined after drying in oven at 120°C until constant weight is reached.